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# THE
# ANALYSIS OF RESINS
## BALSAMS AND GUM RESINS
### WITH A BIBLIOGRAPHY

BY

DR. KARL DIETERICH

OF THE HELFENBERG CHEMICAL WORKS

*TRANSLATED FROM THE GERMAN*

SECOND ENGLISH EDITION, REVISED AND ENLARGED

BY

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# PREFACE

It may be stated without fear of contradiction that the analytical data hitherto published dealing with the many resinous substances are far from being as uniform, accurate, and reliable as in the case of such bodies, for example, as the fats and oils. Even though the resins are, speaking from a chemical point of view, in no way very similar, or nearly allied, to the definitely characterised fats, the great variations in the analytical values obtained are nevertheless remarkable, since the methods of examination have, in both cases, almost without exception, been the same. Although, owing to the crude methods of preparation and diverse commercial usages, the constitution of the resinous substances—by which name the author implies the true resins, balsams, and gum resins—as inconstant, alterable mixtures of amorphous and, for the most part, unknown bodies, is such that no complete concordance of analytical values could be expected, it becomes an interesting, and indeed inevitable, problem to ascertain what are the causes of this lack of concordance; and an additional question also arises, namely, from what points of view should the matter be approached in future with the idea of improving the analytical methods, and thereby securing greater uniformity in the results already obtained?

In the author's opinion, the relatively great fluctuations

in existing results, which the reader will find recorded in the second part of the present work, are principally attributable to the following causes—

I. The methods employed.

II. The use of extracts in place of the natural drugs.

III. The lack of experiments upon authentic pure resins as they come from the parent tree, the results of which researches should constitute a basis of quality.

IV. The lack of individuality in the resins examined, and which for the most part are not met with in an unadulterated state in commerce.

With regard to the first point, it may be said that almost every investigator has hitherto effected the saponification test by a different method. One has boiled the mixture under a reflux condenser, whilst another has allowed the alkali to act during a process of concentration; a third has restricted the operation to a short time, and a fourth extended it over a longer period. Similarly, no uniformity exists in the determination of the acid value, a special method designed for general application to the resinous bodies in question being still wanting. Even though it be erroneous to employ a *single* uniform method for *all* resins —as has latterly been rightly attempted in the case of the fats and oils—and though it appears more advisable to specialise and individualise for each particular resin by itself, nevertheless a *uniform* method is necessary to enable all analysts to work according to well-defined conditions, and not in divergent ways, since slight deviations in the conditions of experiment are particularly liable to lead to great differences in the results when resinous substances are in question. Again, in connection with point II, it has hitherto been the practice of analysts to work exclusively

with extracts and not with the natural drugs themselves. Now it is evident that no reliable opinion on the natural drugs can ever be based upon extracts, owing to the highly divergent composition exhibited by these bodies (the gum resins particularly), in respect of their volatile constituents and substances soluble in alcohol, in consequence of which the saponification value of the extracts can never represent that of the crude products. Moreover, the extracts are so dark in colour that it is difficult to ascertain precisely the moment of change. To come to point III, the number of resinous products hitherto examined in a natural state, *i. e.* as they come from the parent plant, is very small, the commercial products being taken with all their impurities and modifications from the original types. Finally, in connection with point IV, it has been the custom to apply the methods of analysis used for fats and oils to the resinous bodies without taking the special constitution of the latter into consideration, and thus it is that determinations have been made of the ester value and saponification value of resins that contained no esters, acid value of non-acid resins, and so on. If, however, the pure scientific chemistry of the resins be regarded as the foundation for their analytical examination—as in the analysis of other substances—it becomes evident that the recent researches pursued in that subject by Tschirch, his pupils, and other workers, must be incentive to the revision, improvement, and individualisation of the methods of testing now in use for resins.

In this direction the author has endeavoured, by systematic investigation in the analysis of resins, to realise the conditions which he considers valuable for the improvement of the methods, and has hitherto laid down as fundamental rules for his own guidance, viz.—

I. Analysing the natural drugs themselves.
II. Defining uniform regulations for the performance of more rational methods.
III. Individualising these methods, on the basis of the modern chemistry of the resinous bodies.
IV. Selecting quantitative methods in preference to qualitative methods, the colour reactions in particular.
V. Determining standard limits for the various constants, on the basis of investigations performed on authentically pure samples, taken direct from the parent tree.

Bearing these rules in mind, it will not be considered surprising that the author should have modified his method of determining the acid value (for example) to a different degree for almost every separate resin, the value being determined directly in one case, and indirectly, or in some other manner, in another. These modifications are not—as would at first sight appear—arbitrary, but are the result of practical experiments, intended to keep in touch with practice on the one hand, and the modern chemistry of the resins on the other.

Whether this method of procedure is correct or no, time will show. The author believes, nevertheless, that the present work will fill a gap in the literature of the subject, there being no comprehensive book as yet in existence dealing with the widespread researches in the domain of resin analysis, and because the space allotted to the author on this branch, in Lunge's work on chemico-technical methods of examination, was naturally very small, and insufficient to treat the available materials in anything like an exhaustive manner. At any rate, the comprehensive data now published will contribute to the further develop-

ment of the analysis of resins, and form a commencement for establishing definite value limits and methods, in so far as these data show the present state of the subject, and the experience hitherto gained by workers in this branch.

If certain contradictions appear here and there in the experiences now published, reference thereto should not be construed as implying doubt as to the reliability of the authorities concerned, or as laying any blame on the latter, but solely as characterising the prevailing condition of things. It has already been stated that the uniformity of composition of the resins leaves much to be desired, and that external conditions, as well as the age of the sample, have considerable influence on the results of the analytical examination. This is especially true of such resins as dammar, copal, and sandarach, which exhibit oftentimes remarkable differences of solubility, even in the hands of unimpeachable authorities, according to the age and origin of the sample, and the length of time it has been exposed to air and light after exuding from the parent tree. Futhermore, when it is remembered that the acid and saponification values are often empirical, and not theoretically unimpeachable, it will be evident what care must be bestowed on judging and appraising the available materials on the one hand, and how valuable on the other, to the subject of resin analysis, is a large accumulation of experimental, numerical data, and the experience connected therewith.

The prototype kept in mind by the author is the excellent work on *The Analyses of Fats and Waxes*, by Benedikt and Ulzer; the more so that Benedikt expressed the opinion that the analysis of the fats would prove instructive for the analysis of resins.

Although the analysis—*i. e.* testing and determining the

value—of resins forms the main subject of the present work, it was also considered desirable to include the chemical and pharmacognostic data, necessary as a foundation, and to the comprehension of their analysis, especially such of these data as correspond to the most recent state of knowledge. This portion has, however, been restricted to such points as concern the analysis and individualisation of the resins. The pure chemistry of the subject—the special sphere of labour of the Berne Institute, and its director, A. Tschirch —must naturally be reserved, as regards details, for the latter's work on *Resins and Resiniferous Substances*.

The material at the author's disposal has been divided into two main portions—

Part I. General.
Part II. Special.

Of these, the first deals with the definition of the resins, the usual methods of examination, identification, classification, and general properties, as well as with the chemistry, etc., of the constituents of the resins; whilst the second part treats of the resins separately, and describes their—

Origin and habitat.
Chemical constituents on the basis of recent research.
General properties and commercial varieties.
Adulterations and substitutions.
Analysis and evaluation.
Literature, referring solely to analysis, in order to facilitate the consultation of the original reports.

In using this special part for the analytical testing of resins, special attention is directed to the Introduction, the General Remarks, and Definitions, and, above all, to the methods of analysis. In addition, a brief notice of the method is given in each case, with particular information as to whether the natural product or only a portion

(alcoholic extract in alcoholic solution, etc.) of the resin was examined.

The calculation of the values found by the author's own methods has been carried out on the basis of the table of atomic weights determined recently by Landolt, Ostwald, and Seubert, and accepted by the German Chemical Society.

Where practicable, colloquial nomenclature has been adopted for the various resins instead of the Pharmaceutico-Latin names, though the latter have been retained in such cases as galbanum, ammoniacum, where no colloquial term has come into general use.

There being as yet no thorough classification possible on purely chemical lines, the subdivision into—

A. Balsams,
B. Resins,
C. Gum Resins,

has been retained in the special part.

Finally, it is the author's welcome duty to record his thanks to those who have given assistance to his task. This applies, in the first place, to his chief assistant—of many years' standing—Mr. H. Mix, who has rendered valuable service in collecting literary matter, reading proofs, and in numerous practical researches, etc. Furthermore, thanks are due to Professor Dr. A. von Vogl, who was good enough—through the kind mediation of Mr. A. Kremel—to enrich the author's collection of resins by exchanges with the Viennese pharmacognostical collection; also, to Messrs. Gehe & Co. (Dresden), Worlée & Co. (Hamburg), and E. & H. Oldendorf (London), for having kindly supplied, for examination, numerous samples of rare resins or commercial varieties.

It is hoped that the present work will meet with a good reception, as forming a decided contribution towards the

characterisation of the resinous bodies; and that the collaboration of colleagues will enable a second edition to record real progress and improvement in the analytical examination of these bodies—progress that will bring us soon to the goal of resin analysis, viz. *the definite establishment of rational methods and limits of valuation for the constants.*

KARL DIETERICH.

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# ABBREVIATIONS IN BIBLIOGRAPHY

| | |
|---|---|
| *Amer. Jour. Pharm.* | American Journal of Pharmacy. |
| *Ann. de Chim.* | Annales de Chimie. |
| *A. d. Ph.*<br>*Arch. Pharm.* | Archiv der Pharmacie. |
| *Ann. Rep. India Museum* | Annual Reports of the India Museum. |
| *Ap. Ztg.* | Apotheker Zeitung. |
| *Ap. Ztg. R.* | Apotheker Zeitung Repertorium. |
| *Ber.* | Berichte der Deutschen Chemischen Gesellschaft. |
| *Bull. Imp. Inst.* | Bulletin of the Imperial Institute. |
| *Bull. Soc. Chim.* | Bulletin de la Société Chimique de France. |
| *Chem. Centrl.* | Chemischer Zentralblatt. |
| *Chem. Neus* | Chemical Neus. |
| *Chem. Rev.*<br>*Chem. Rev. Fett v Harz Indt.* | Chemische Revue über die Fett und Harz Industrie. |

| | |
|---|---|
| *Compt. Rend.* | Comptes-Rendus hebdomadaires de Séances de l'Académie des Sciences. |
| *D. d. H. A.* | Decennium der Helfenberger Annalen. |
| *Dingler's Poly. Jour.* | Dingler's Polytechnicher Journal. |
| *D. A. III.* | Deutsche Arzneibuch III. |
| *Gazetta Chim.* | Gazetta Chimica Italiana. |
| *Gmelin's Handb. d. Chem.* | Gmelin's Handbuch der Chemie. |
| *H.A.* | Helfenberger Annalen. |
| *Hand. de. Chem.* | Handbuch der Chemie. |
| *I.D.* | Inaugural Dissertation. |
| *J. Amer. Chem. Soc.* | Journal of the American Chemical Society. |
| *J. Franklin Inst.* | Journal of the Franklin Institute. |
| *J. Ind. Eng. Chem.* | Journal of Industrial and Engineering Chemistry. |
| *J. Pharm. et de Chem.* | Journal de Pharmacie et de Chimie. |
| *J. Prac. Chem.* | Journal für practische Chemie. |
| *J.S.C.I.*<br>*Jour. Soc. Chem. Indt.* | Journal of the Society of Chemical Industry. |
| *Linn. Trans.* | Transactions of the Linnean Society. |
| *Monatsch. f. Chem.* | Monatschifte für Chemie. |
| *Monit. Scient.* | Moniteur Scientifique. |
| *N.Z.P.D.A.* | Notizen Zur Prufung der Arzneinmittel. |
| *Oest. Ch. Ztg.* | Oesterreiches Chemiker-Zeitung. |
| *Oil & Col. Trades Jour.* | Oil and Colour Trades Journal. |
| *Oil & Colour Trades Jour. Diary* | Oil and Colour Trades Journal Diary. |
| *Pharm. C.* | Pharmaceutische Centralhalle. |
| *Pharm. Jour.* | Pharmaceutical Journal. |
| *Pharm. P.* | Pharmaceutische Post. |
| *Pharm. Tabel.* | Pharmaceutische Tabellen. |
| *Ph. Ztg.* | Pharmaceutische Zeitung. |
| *Pharm. Zent.* | Pharmaceutische Zentralhalle. |
| *Philippine Jour. Soc.* | Philippine Journal of Science. |
| *Proc. Am. Pharm. Assoc.* | Proceedings of the American Pharmaceutical Association. |
| *Proc. Penn. Pharm. Assoc.* | Proceedings of the Pennsylvania Pharmaceutical Association. |
| *R.E.* | Real Encyclopædia. |
| *Rép. de Pharm.* | Répertoire de Pharmacie. |
| *Schimmel's Rep.* | Schimmel's Annual Report. |
| *Sudd. Ap. Ztg.* | Süddeutsche Apotheker-Zeitung. |
| *Wien. Akad. d. Wiss.* | Wien Akademie der Wissenchaft. |
| *Wochenbl. Papierfab.* | Wochenblad-Papierfabrikant. |
| *Z. Angew. Chem.*<br>*Z. f. Angew. Chem.* | Zeitschrift für Angewandte Chemie. |

# ANALYSIS OF RESINS

## PART I

### GENERAL

**Definition of Resins in General.**—The terms "resins" and "resinous substances" generally, are applied to certain secretion or excretion products of plants, formed during the course of metabolism, partly due to normal phenomena, and partly to the influence of disease.

Formerly, the resins were regarded as conversion products of the tannic acids and phlobaphenes, or even as precursors of the ethereal oils (Dragendorff),[1] but the tendency at present is rather to consider the phlobaphenes as oxidation products of glucoside resinotannic acids, and the resins as oxidation products of the ethereal oils. According to Wallach the terpenes in particular appear to stand in close relation towards these secretions. As to what substances are actually drawn upon in the plant in order to form resins no definite conclusions can yet be formulated. That oxidation processes play a considerable part, both in the plant before and after exudation of the secretion, and also after the collection and storage [2] of the same in contact with air and

[1] *A. d. Ph.*,1879, vol. 15, p. 50.

[2] See Kiessling, Weger, and Lippert, on "Oxygen Absorption by Resins": *Chem. Rev.*, 98, I. 286; *Zeits. f. angew. Chem.*, 98, I. 1248; and Weger's pamphlets published in 1899 (Baldamus, Leipzig).

light, has recently been proved by K. Dieterich,[1] to demonstration. According to this report, the resins and resinous products which we are familiar with are, for the most part, secondary products, differing materially from the excretion products and products of the degradation of complex molecular compounds, as constituted within the tree or at the moment of exudation. Consequently, before reaching us as commercial products, the resins have really passed through three stages of modification, in each of which different influences have modified the composition of the mixtures. The secretion, while within the tree, *i. e.* in the primary stage, exhibits a very different composition to that which it does after exudation and exposure to light and air—a change externally made evident by the hardening of the product and by its altered colour. The manipulations which follow in the recovery of these products—melting, extracting, etc.—cause further changes, the result being that commercial resins are really secondary and tertiary mixtures. Consequently, as mentioned in the Preface, it is of particular importance to the attainment of a knowledge of the resins that authentically pure samples, taken direct from the parent plant, should be examined, in order that rational methods of testing, and normal values, may be established. Unfortunately this has hitherto been impossible, except in the case of very few resins and balsams (Peru balsam, benzoin, storax, etc.). In any event, the resins—in contradistinction to the fats, which are mostly synthetical products —should be regarded as oxidation and condensation products—in fact, as degradation products of complex molecular compounds, by oxidation, or as condensation products of complex molecular compounds. That this is the general view is proved—to give only a limited number of examples—

[1] *H. A.*, 1896, pp. 15 *et seq.*

on the one hand, by the earlier attempts at the artificial synthesis of resins from Venice turpentine and fuming sulphuric acid (Voges, especially in the preparation of artificial incense); further, from ethereal oils and anhydrous phosphoric acid (Hlasiwetz); the artificial preparation of caoutchouc from turpentine oil and gaseous hydrochloric acid; and, on the other hand, the condensation experiments of Döbner and Lücker for the production of an artificial guaiacum resin, and, lastly, the condensation experiments of A. von Bayer for preparing undefined resinous products from aldehydes and phenols.

From the physical aspect we apply the terms "resin" and "resinous substance" to products which exhibit an amorphous (rarely a crystalline, but often a glassy) structure; some are hard and brittle, others are soft and sticky, but they are all fusible, burn with a smoky flame, are largely or entirely insoluble in water, and—unlike the fats and oils—leave no greasy streak on paper; are more or less saponifiable, not liable to rancidity, and constitute mixtures of various coloured and colourless, solid and liquid, aromatic and inodorous constituents. Since the number of uniform products—such as colophony ("rosin")—which contain resin alone, without any gums, ethereal oils, or any large proportion of other important constituents, is small, the general term "resin" has been applied to a large number of mixtures, consisting of aggregations of the pure substance with vegetable and mineral impurities, which are further distinguished by the names—Balsams, Gum Resins, and True Resins. In fact, it has been proposed by some to include with the resins certain vegetable saps, such as aloes and catechu, containing only a relatively small proportion of resin.

**Definition of the Balsams, and especially the Gum Resins.**—By *balsams* we understand resinous mixtures

which contain the resin dissolved or emulsified in ethereal oils; these are more or less fluid, and usually exhibit a strong, specific odour. *Gum resins* are mixtures of substances such as gums, extracts, bitter principles, resin, etc., which, being in themselves only partially soluble in any one fluid, the complex is partly soluble in water, and partly in alcohol or ether, besides which they may contain ethereal oils, in addition to resin and gums, their consistence therefore varying according to the relative proportions of the different constituents.

**External and Superficial Characteristics of Resinous Products.**—Wiesner [1] thoroughly investigated this question, and found that the condition of the surface is influenced by solidification or weathering, or the two conjoined. Thus the "goose skin" of copal is due to weathering. In the gum resins—Flückiger's opinion notwithstanding—there is no homogeneity of surface or admixture, but they mostly consist of gums enclosing droplets of resin and oil. Thus gamboge, for example, is a hyaline mass with embedded drops of resin and oil. With regard to the individual types (gamboge, ammoniacum, and galbanum type; asafœtida, olibanum, and myrrh type) and special individuals, see Wiesner (*l.c.*).

**Distinction between Resinous Bodies and the Fats and Oils.**—As previously mentioned, the resins differ from the fats and oils even in their origin. The fats are mostly of synthetic origin, the resins formed generally by degradation or condensation. Whereas the fats and oils, being all glycerides of the fatty acids, constitute substances of definite character, the resinous bodies are variable and impure mixtures of substances the composition of which is for the most part but little known.

[1] *Zeits. d. Allgem. Oestr. Apoth.-Ver.*, 1899, Nos. 16 and 18.

Furthermore, it is noteworthy that in the hydrolytic decomposition of the fats and oils, which represent esters of the fatty acids, the acids are obtained in excess whilst the alcohols (glycerin) are in smaller quantity. On the other hand, the esteriferous resins corresponding to the fats mostly yield but very small amounts of aromatic or resin acids, with a far larger proportion of alcohols (resinols and resinotannols). However, despite these great genetic and chemical differences, the methods employed for the examination of the oils and fats have, almost without exception, been also applied to the resinous substances.

**Origin, Occurrence, and Collection of Resinous Substances.**—These substances, as already remarked, are secretions, or excretory products from resiniferous trees and plants, and exude to some extent naturally therefrom as a physiological phenomenon, though for the most part they are collected as a result of wounds due to the treatment by man. According to the researches of Tschirch, Möller, and others, nearly all the resins, gum resins, and balsams are formed in special secretory glands; the solid resins, such as furnished by the *Umbelliferæ*, *e. g.* asafœtida, ammoniacum, etc., being exuded by the epithelial cells into the so-called chizogenic glands, whilst the balsams are formed in the lysigenic oil cavities by the dissolution of the cell membranes. Just as external treatment by the hand of man is able to convert the physiological excretion of the resins into a pathological phenomenon, a similar excessive pathological secretion, *e. g.* the malady of "gummosis" in certain gum trees, may occur in the absence of external influences. Particularly numerous and important resinous products—gum resins especially—are furnished by the *Umbelliferæ* and *Burseraceæ*, while the varieties *Pinus* and *Larix* also yield a large number of resins; we are indebted also to the

*Cæsalpinaceæ* for some very important balsams. Few of the resiniferous trees are indigenous to Europe, whereas America supplies a great many resinous products; the same may be said of Africa and Asia—Persia and Asia Minor especially. Of the gum resin trees none to speak of are indigenous to Europe, and but few resins, such as pine resin, turpentine, and one or two others; therefore this lack of material at first hand is a great drawback to the attainment of accurate information on the collection, original composition, and real origin of the resins, all of which points still remain to some extent in obscurity. Finally, when it is borne in mind the great distances and large number of hands through which these products have to pass, it will cease to be surprising to find that the products reach us in a totally altered, variable, and, above all, adulterated condition. To mention only one point, the methods of collecting resins, such as cutting the trees, boiling the twigs and branches, concentrating the extract, etc., are so crude and variable that the resulting products must of necessity exhibit irregularities in their properties, etc.

**Classification.**—On the basis of physical properties the resinous substances can be classified into balsams, resins, and gum resins. And at the present time, when the chemistry of these bodies is by no means complete, although progressing, and when only such resins as have been more closely investigated can be subjected to chemical classification, the physical method remains the most suitable and practical, notwithstanding its lack of absolute precision and the frequent occurrence of intermediate members and transition grades. Up to a certain point, however, chemical classification has been rendered possible by the classical and systematic labours of Tschirch and his pupils, at least in so far as it concerns the resin products hitherto subjected to

careful examination; and the following classification has been proposed by K. Dieterich on the basis of Tschirch's investigations:—

1. Resins which consist of esters of the aromatic series, and either contain or do not contain free acids—*e. g.* benzoin, dragon's-blood, acaroid resin, etc.
2. Resins consisting of esters of specific resin acids, and usually containing, in addition, free resin acids—*e. g.* turpentine, mastic, succinite, elemi, etc.
3. Resins which are not esters, but contain only free resin acids, occasionally accompanied by inert admixtures. To this class belong colophony, copal, guaiacum, sandarach, dammar, etc.

In addition, the author also proposed to group the resinous substances according to the mode of collection pursued, *i. e.* natural (physiological excretion) and artificial (pathological excretion).[1] To the first group would belong all such resins as—*e. g.* dragon's-blood—exude naturally from the tree without human interference; and to the other class, all such as are collected after wounding, heating, etc.—the quantities so obtained being far greater than those recoverable by the natural method. This latter category, in fact, now comprises nearly the entire series of the resins, artificial means being necessarily resorted to for the systematic collection of these substances.

Fr. Lewton proposes to classify the resinous substances as follows:—[2]

[1] *H. A.*, 1896, pp. 33 *et seq.*

[2] It should be stated that this classification, based on physical and chemical characteristics, is not altogether free from objection; furthermore, that the characteristics based on solubility do not quite coincide with present-day experience. The table is reproduced here for the sake of completeness, and it is worthy of attention, despite sundry deficiencies.

True Resins.—Vegetable substances, hard, pulverulent, resembling gum in outward appearance, neither soluble in, nor softened by, cold water. They burn with a bright, smoky flame, and contain much C, little O, and no N.

Chemical composition difficult to define; usually mixtures of resin acids.

*Sub-groups :—*

($\alpha$) Copal group.—These will not dissolve in the usual solvents unless they have been previously fused.

($\beta$) Dammar group.—More or less soluble in ether, chloroform, benzene, acetone, turpentine oil, etc., but quite insoluble in alcohol.

($\gamma$) Sandarach group.—More or less soluble in alcohol without the application of heat. Guaiacum also belongs to this group.

($\delta$) Colophony group.—Entirely soluble in alcohol.

($\varepsilon$) Benzoin group.—Soluble in alcohol. Liberate benzoic or cinnamic acid when heated.

($\theta$) Shellac group.—Resinous excretions caused by insect punctures. Form a turbid solution in alcohol.

Inodorous Gum Resins.—Vegetable excretions, destitute of volatile oils, and consisting of variable mixtures of gums and resin. They furnish an emulsion with water. Gamboge belongs to this class.

Aromatic Gum Resins.—Resembling the above, but containing ethereal oils.

*Sub-groups :—*

($\alpha$) Asafœtida group.—Mostly derived from umbelliferous plants, and give off a disagreeable smell. In addition to asafœtida, the group comprises galbanum, ammoniacum, and opopanax.

($\beta$) Myrrh group.—These have a more or less agreeable aroma, and are, for the greater part, derived from the *Burseraceæ*. Examples: Myrrh, olibanum, bdellium.

Oil Resins.—Vegetable excretions, consisting of resins and volatile oils, the former being frequently in solution in the latter, and therefore liquid.

*Sub-groups :—*

($\alpha$) Varnish group.—Produce a shiny coating when applied to any surface. Mostly derived from plants of the *Anacardiaceæ* family.

($\beta$) Copaiba group.—Sweet-smelling liquids, mostly classified with the balsams, but differing therefrom by containing less resin.

($\gamma$) Turpentine group.—Comprises the soft resins, containing larger or smaller amounts of volatile oils. Derived from *Coniferæ*.

($\delta$) Elemi group.—Soft resins, rarely containing above 10 per cent. of ethereal oil. Derived from *Burseraceæ*.

True Balsams.—Vegetable excretions, consisting of resin, aromatic acids, alcohols, and esters. Examples: Peruvian balsam, Tolu balsam, and liquid storax.

**Chemical Constituents of Resinous Substances.**—With regard to these and their characteristics, the main features have been recorded by Tschirch [1] as follows :—

[1] In view of the circumstance that Prof. Tschirch is bringing out a work on resins and resiniferous plants, which will deal with the chemistry of the subject, the present author confines himself to a brief résumé of Tschirch's researches, referring the reader to that authority's own book for fuller details.

1. He finds the main constituents to be—

(*a*) Resin esters (resins) or their products.
(*b*) Resin acids (resinolic acids).
(*c*) Resenes, indifferent substances of unknown classification.

Very few resins contain representatives of all three groups, the majority being either ester resins, resinolic acid resins, or resene resins.

Aroma, when present, is influenced by ethereal oils, aldehydes, or very small quantities of liquid esters, among which cinnamic acid esters, and especially the phenylpropyl ester of this acid, play a part.•

2. The *aromatic acids* forming resin esters, or resins, appear to be mutually related, and are divisible into two classes, one of which is derived from benzoic acid, and the other from cinnamic acid.

I. Benzoic acid : $C_6H_5COOH$ (Peruvian balsam, Tolu balsam, Siam benzoin, dragon's-blood).

Benzoylacetic acid :

$$CH_2(C_6H_5CO)COOH \text{ (dragon's-blood).}$$

Salicylic acid :

$$C_6H_4{<}\begin{matrix}OH\ (1)\\COOH\ (2)\end{matrix}$$

(Ammoniacum).

II. Cinnamic acid : $C_6H_5.CH = CH.COOH$ (Tolu balsam, Peruvian balsam, storax, Sumatra benzoin, yellow acaroid resin).

[$\beta$-Phenylhydracrylic acid :

$$C_6H_5C(OH) = CH.COOH$$

(Phenyl-$\beta$-mono-oxy-acrylic acid)
(probably in dragon's-blood).]

| Name of Acid. | Formula. | Melting Point. | Source. | Authority. |
|---|---|---|---|---|
| Formic | $CH_2O_2$ | — | Heerabol myrrh | O. von Friedrichs |
| Acetic | $C_2H_4O_2$ | — | ,, ,, | ,, ,, |
| Caproic | $C_6H_{12}O_2$ | — | Ammoniacum | — |
| Benzoic | $C_7H_6O_2$ | 121° | Siam benzoin | — |
| Salicylic | $C_7H_6O_3$ | 155° | Ammoniacum | — |
| Umbellic | $C_8H_7O_3$ | — | Galbanum | — |
| Cinnamic | $C_9H_8O_2$ | 133° | Sumatra benzoin | — |
| | | | Peru and Tolu balsams | — |
| Paracoumaric | $C_9H_8O_3$ | — | Acaroid resin | Bamberger |
| Caffeic | $C_9H_8O_3$ | — | Resin of pinus | ,, |
| Ferulaic | $C_9H_9O_4$ | — | Opoponax | Tschirch |
| a-Dibasic acid | $C_9H_{12}O_2$ | — | Bisabol myrrh | Tucholka |
| ,, | $C_9H_{12}O_2$ | — | ,, | ,, |
| ,, | $C_{13}H_{16}O_8$ | — | Heerabol myrrh | ,, |
| Aleuritic | $C_{13}H_{26}O_4$ | 101°–105° | Shellac | Tschirch and Farner |
| α-Commiphoric | $C_{14}H_{18}O_4$ | 201°–203° | — | — |
| β-Commiphoric | $C_{14}H_{18}O_4$ | 205° | — | — |
| α-ψ-Euphorbonic | $C_{14}H_{22}O_{10}$ | 112°–113° | False euphorbium | Tschirch and Leuchtenberger |
| α-Heerabo-myrrholic | $C_{15}H_{22}O_7$ | 220°–225° | Heerabol myrrh | — |
| Laccainic | $C_{16}H_{12}O_8$ | — | Shellac | Tschirch and Farner |
| Agaric | $C_{16}H_{30}O_5 + H_2O$ | 138°–139° | Ammoniacum | Jahns |
| γ-Commiphoric | $C_{17}H_{22}O_5$ | 169°–170° | | — |
| Myrrholic acid | $C_{17}H_{22}O_5$ | 236° | Heerabol myrrh | O. von Friedrichs |
| β-ψ-Euphorbonic | $C_{18}H_{22}O_{12}$ | 81° | False euphorbium | Tschirch and Leuchtenberger |
| Homo-para-copaibic | $C_{18}H_{28}O_3$ | 111° | — | — |
| a-Dibasic acid | $C_{18}H_{33}O_3$ | — | Dammar | B. Graf |
| ψ-Euphorbic | $C_{24}H_{36}O_6$ | 108°–109° | False euphorbium | Tschirch and Leuchtenberger |
| Euphorbic | $C_{24}H_{30}O_6$ | 107°–108° | Euphorbium | Tschirch and Paul |
| a-Dibasic acid | $C_{26}H_{32}O_9$ | — | Heerabol myrrh | Tucholka |
| Commiphorinic | $C_{28}H_{36}O_8$ | 135° | — | — |
| Gambogin or Gambogic | $C_{30}H_{56}O_6$ | 75°–80° | Gamboge | Buchner |
| Boswellic | $C_{32}H_{52}O_4$ | 150° | Olibanum | Tschirch and Halbey |

p-Cumaric acid :

$$C_6H_4 \begin{cases} OH\ (1) \\ CH = CH.COOH\ (4) \end{cases}$$

(yellow and red acaroid).

Ferulaic acid :

$$C_6H_3 \begin{cases} OH\ (1) \\ OCH_3\ (2) \\ CH = CH.COOH\ (4) \end{cases}$$

(Asafœtida).

Umbellic acid :

$$C_6H_3 \begin{cases} OH\ (1) \\ OH\ (3) \\ CH = CH.COOH\ (4) \end{cases}$$

and its anhydride, umbelliferon (in asafœtida, galbanum, sagapenum).

The aromatic acids forming resin esters are therefore mostly oxyacids. Of the fatty acids only the resin ester of succinic acid (amber) has hitherto been observed, but butyric and acetic acid in the free state have been detected in small quantities. A more complete list of the aromatic and other acids found in resins is appended.

3. The *resin alcohols* forming resin esters are either colourless : resinols—in which case they do not give the tannin reaction ;—or are coloured, and answer to the tannin reaction : resinotannols.

*A*. **Resinols.**—About seventeen members of this series are known.

Of the resinols, storesinol is certainly allied to benzoresinol, the spectrum analysis of the solutions in concentrated sulphuric acid placing this beyond doubt. If the simple formula be taken as a basis there is absolutely no difference in percentage composition between succinoresinol and storesinol. Hence these substances are apparently related to one another. All the resinols belong to the aromatic series.

## RESINOLS

| Name of Alcohol. | Formula. | Melting Point. | Source. | Observers. |
|---|---|---|---|---|
| Succinoresinol | $C_{12}H_{20}O$ | 275° | Amber | Tschirch and Aweng |
| Storesinol | $C_{12}H_{20}O$ and $C_{16}H_{26}O$ | — | Storax | von Miller |
| Lariciresinol | $C_{16}H_{19}O_4$ and $C_{19}H_{22}O_2$ | 169° | Larch resin | Bamberger and Landseidel |
| Benzoresinol | $C_{16}H_{26}O_2$ | 274° | Benzoin | Tschirch and Lüdy |
| Honduresinol | $C_{16}H_{26}O_2$ | 286° | White Peru balsam | Thoms and Biltz |
| Pinoresinol | $C_{18}H_{18}O_6$ and $C_{19}H_{20}O_6$ and $C_{19}H_{28}O_4$ | 80°–90° | Pine resin<br>—<br>Fir resin | Bamberger and von Miller<br>—<br>Tschirch and Wegel |
| Chironol | $C_{28}H_{48}O$ | 173°–176° | Burseraceous opoponax | Tschirch and Baur |
| α-Amyrin | $C_{30}H_{50}O$ | 181°–181·5° | Elemi | Vesterburg |
| β-Amyrin | $C_{30}H_{50}O$ | 193°–194° | ,, | ,, |
| α-Caramyrin | $C_{30}H_{50}O$ | 181° | Carana elemi | Tschirch and Saal |
| β-Caramyrin | $C_{30}H_{50}O$ | 192° | ,, | ,, ,, |
| α-Tacamyrin | $C_{30}H_{50}O$ | 181° | Tacamahaca elemi | ,, ,, |
| β-Tacamyrin | $C_{30}H_{50}O$ | 192° | ,, ,, | ,, ,, |
| α-Colamyrin | $C_{30}H_{50}O$ | — | Colophonia elemi | ,, ,, |
| β-Colamyrin | $C_{30}H_{50}O$ | — | ,, ,, | ,, ,, |
| α-Storesinol | $C_{36}H_{58}O_3$ | — | — | — |
| β-Storesinol | $C_{36}H_{58}O_3$ | — | — | — |

*B.* **Resinotannols.**—The following are known :—

Siaresinotannol : $C_{12}H_{13}O_2(OH)$, in Siam benzoin (Tschirch and Lüdy).

Sumaresinotannol : $C_{48}H_{19}O_3(OH)$, in Sumatra benzoin (Tschirch and Lüdy).

Peruresinotannol : $C_{18}H_{19}O_4(OH)$, in Peruvian balsam (Tschirch and Trog).

Toluresinotannol : $C_{17}H_{17}O_4(OH)$, in Tolu balsam (Tschirch and Oberländer).

Galbaresinotannol : $C_{18}H_{29}O_2(OH)$, in galbanum (Tschirch and Conrady).

Ammoresinotannol : $C_{18}H_{29}O_2(OH)$, in ammoniacum (Tschirch and Luz).

Sagaresinotannol : $C_{24}H_{27}O_4(OH)$, in sagapenum (Tschirch and Hohenadel).

Dracoresinotannol : $C_8H_9O.(OH)$, $[C_{24}H_{30}O_4]$, in palm dragon's-blood (Tschirch and K. Dieterich).

Panaxresinotannol : $C_{34}H_{49}O_7(OH)$ $[C_{17}H_{25}O_4]$ in burs. opopanax (Tschirch and Baur).

Xanthoresinotannol : $C_{43}H_{46}O_{10}$, in yellow acaroid (Tschirch and Hildebrand).

Erythroresinotannol : $C_{40}H_{40}O_{10}$, in red acaroid (Tschirch and Hildebrand).

On comparing these formulæ, the first thing which strikes the eye is that eight of the resinotannols contain multiples of six carbon atoms—Asaresinotannol, galbaresinotannol, oporesinotannol, siaresinotannol, sumaresinotannol, peruresinotannol, ammoresinotannol, and sagaresinotannol.

Furthermore, it is evident that galbaresinotannol and ammoresinotannol have the same percentage composition, and that peruresinotannol differs from sumaresinotannol by merely a single oxygen atom. There are, however, other points of resemblance. Thus peruresinotannol is a homologue

| Author and Source. | Tannol. | Formula. | % C. | % H. | Acetylation. | Benzoylation. | Treatment with $HNO_3$. | Potash Fusion Test. |
|---|---|---|---|---|---|---|---|---|
| Tschirch and Pedersen (Aloe) | Aloresinotannol | $C_{22}H_{26}O_6$ | 68·39 | 6·73 | — | $C_{23}H_{24}O_6(C_6H_5CO)_2$ | — | — |
| Tschirch and Luz (Ammoniacum) | Ammoresinotannol | $C_{18}H_{30}O_3$ | 73·45 | 10·20 | $C_{18}H_{29}O_3 . CH_3CO$ | $C_{18}H_{29}O_3(C_6H_5CO)$ | Styphnic acid | Resorcin |
| Tschirch and Polasek (Asafœtida) | Asaresinotannol | $C_{24}H_{34}O_5$ | 71·43 | 8·69 | $C_{24}H_{33}O_5 . CH_3CO$ | $C_{24}H_{33}O_5(C_6H_5CO)$ | Picric acid | — |
| Tschirch and Lüdy (Sumatra benzoin) | Sumaresinotannol | $C_{18}H_{20}O_4$ | 72·00 | 6·66 | — | — | Picric acid | Protocatechuic acid |
| Tschirch and Lüdy (Siam benzoin) | Siaresinotannol | $C_{12}H_{14}O_3$ | 70·01 | 7·01 | $C_{12}H_{13}O_3 . CH_3CO$ | — | Picric acid | — |
| Tschirch and Conrady (Galbanum) | Galbaresinotannol | $C_{18}H_{30}O_3$ | 73·45 | 10·22 | $C_{18}H_{29}O_3 . CH_3CO$ | $C_{18}H_{29}O_3(C_6H_5CO)$ | Camphoric and Camphoronic acids | — |
| Tschirch and Baur (Burs. opopanax) | Panaxresinotannol | $C_{34}H_{50}O_8$ | 69·62 | 8·53 | — | — | — | — |
| Tschirch and Trog (Peru balsam) | Peruresinotannol | $C_{18}H_{20}O_5$ | 68·30 | 6·30 | $C_{18}H_{19}O_5 . CH_3CO$ | $C_{18}H_{19}O_5(C_6H_5CO)$ | Oxalic and Picric acids | — |
| Tschirch and Knitl (Umb. opopanax) | Oporesinotannol | $C_{12}H_{14}O_3$ | 69·83 | 6·83 | — | $C_{12}H_{13}O_3(C_6H_5CO)$ | Oxalic and Picric acids | — |
| Tschirch and Hohenadel (Sagapenum) | Sagaresinotannol | $C_{24}H_{28}O_5$ | 72·70 | 7·07 | $C_{24}H_{27}O_5 . CH_3CO$ | $C_{24}H_{27}O_5(C_6H_5CO)$ | Styphnic acid | — |
| Tschirch and Oberländer (Tolu balsam) | Toluresinotannol | $C_{17}H_{18}O_5$ | 67·50 | 5·96 | $C_{17}H_{17}O_5 . CH_3CO$ | $C_{17}H_{17}O_5(C_6H_5CO)$ | Picric and Oxalic acids | Protocatechuic acid |
| Tschirch and Oberländer (Red acaroid) | Erythroresinotannol | $C_{40}H_{40}O_{10}$ | — | — | — | — | — | — |
| Hildebrand (Yellow acaroid) | Xanthoresinotannol | $C_{43}H_{46}O_{10}$ | — | — | — | — | — | — |
| Tschirch and Lüdy (Sumatra benzoin) | Benzoresinotannol | $C_{18}H_{20}O_4$ | — | — | — | — | — | — |
| Tschirch (Dragon's blood) | Dracoresinotannol | $C_8H_{10}O$ | — | — | — | — | — | — |

## CONSTITUENTS OF RESINS AND BALSAMS

### Resinolic Acids

| Name of Acid. | Formula. | Melting Point. | Source. | Observer. |
|---|---|---|---|---|
| Mancopalic | $C_8H_{12}O_2$ | 175° | Manila copal | Tschirch and Stephan |
| Mancopalenic | $C_8H_{14}O_2$ | 100°–105° | ,, | ,, ,, |
| α-Jeffropinic | $C_{10}H_{14}O_2$ | 160°–161° | Pinus Jeffryi | Tschirch and Leuchtenberger |
| β-Meta-copaivic | $C_{10}H_{16}O_2$ | 89°–90° | Maracaibo balsam | Tschirch and Keto |
| Kaurinic | $C_{10}H_{16}O_2$ | 192° | Kauri | Tschirch and Stephan |
| α-Mancopalolic | $C_{10}H_{18}O_2$ | 85°–90° | Manila copal | ,, ,, |
| β-Mancopalolic | $C_{10}H_{18}O_2$ | 83°–88° | ,, | ,, ,, |
| α-Accracopalenic | $C_{10}H_{20}O_2$ | 142°–146° | Accra copal | — |
| β-Jeffropinic | $C_{12}H_{18}O_2$ | 80°–82° | Pinus Jeffryi | Tschirch and Leuchtenberger |
| α-Kaurolic | $C_{12}H_{20}O_2$ | 81°–83° | Kauri | Tschirch and Stephan |
| β-Kaurolic | $C_{12}H_{20}O_2$ | 85°–87° | ,, | ,, ,, |
| β-Accracopalenic | $C_{12}H_{20}O_3$ | 150°–152° | Accra copal | — |
| Kauronolic | $C_{12}H_{24}O_2$ | 86°–89° | Kauri | Tschirch and Stephan |
| Loangocopalolic | $C_{12}H_{34}O_2$ | 60° | Abies pectinata | Tschirch and Willner |
| Abienic | $C_{13}H_{20}O_2$ | 114°–115° | Strasburg turps | Tschirch and Weigel |
| Pimarinic | $C_{13}H_{20}O_2$ | — | — | — |
| Picea-pimarinic | $C_{13}H_{20}O_2$ | 132°–135° | Jura turps | Tschirch |
| Palabieninic | $C_{13}H_{20}O_2$ | — | Pinus palustris | ,, |
| Sandaracolic | $C_{13}H_{20}O_2$ or $C_{45}H_{66}O_7$ | 140° | — | Tschirch and Balzer |
| Beljiabieninic | $C_{13}H_{22}O_2$ | — | Russian white pitch | Tschirch |
| Silveolic | $C_{14}H_{20}O_2$ | 138° | Finland turps | ,, |
| Pimarinic | $C_{14}H_{20}O_2$ | — | Bordeaux turps | ,, |
| α-Jeffropinolic | $C_{14}H_{20}O_2$ | 117°–118° | — | Tschirch and Leuchtenberger |
| β-Jeffropinolic | $C_{14}H_{20}O_2$ | 77°–78° | — | — |
| Pimaric or Pimarinic | $C_{14}H_{22}O_2$ | — | — | — |
| Leonecopalinic | $C_{14}H_{24}O_2$ | 184° | Sierra Leone copal | Tschirch and Willner |
| Abietolic (?) | $C_{16}H_{24}O_2$ | — | — | — |
| Accracopalinic | $C_{14}H_{26}O_3$ | 122°–124° | Accra copal | — |
| β-Loangocopalic | $C_{15}H_{30}O_2$ | 60° (about) | Loango copal | Tschirch and Willner |
| α-Benicopalolic | $C_{15}H_{32}O_6$ | 81° | Benin copal | — |
| Callitrolic | $C_{15}H_{20}O_2$ or $C_{30}H_{48}O_5$ or $C_{65}H_{84}O_8$ | — | Sandarac | — |
| | | — | — | T. A. Henry |
| | | 248° | — | Tschirch and Balzer |

| | | | | |
|---|---|---|---|---|
| Tacamaholic | $C_{15}H_{25}O_2$ | 104°–106° | Tacamahac | Tschirch and Saal |
| α-Silvinolic | $C_{15}H_{26}O_2$ | 85°–90° | Finland turps | Tschirch |
| β-Silvinolic | $C_{15}H_{26}O_2$ | 89°–95° | ,, | ,, |
| β-Benicopalinic | $C_{15}H_{28}O_2$ | 193°–197° | Benin copal | — |
| α-Abietinolic | $C_{16}H_{24}O_2$ | 95°–96° | Strasburg turps | Tschirch and Weigel |
| β-Abietinolic | $C_{16}H_{24}O_2$ | 93°–94° | ,, | ,, |
| α-Palabietinolic | $C_{16}H_{24}O_2$ | — | Pinus palustris | Tschirch |
| β-Palabietinolic | $C_{16}H_{24}O_2$ | — | ,, | ,, |
| α-Beljiabietinolic | $C_{16}H_{24}O_2$ | — | Russian white pitch | ,, |
| b-Beljiabietinolic | $C_{16}H_{24}O_2$ | — | ,, | ,, |
| Podocarpic | $C_{17}H_{28}O_3$ | 187°–188° | Podocarpin resin | Oudemann's |
| Benincopalic | $C_{17}H_{32}O_4$ | 137° | Benin copal | — |
| Kaurinolic | $C_{17}H_{34}O_2$ | 128°–130° | Kauri | Tschirch and Stephan |
| α-Pimarolic | $C_{18}H_{26}O_2$ | 90°–91° | Bordeaux turps | Tschirch |
| β-Pimarolic | $C_{18}H_{26}O_2$ | — | ,, | ,, |
| α-Larinolic | $C_{18}H_{26}O_2$ | 80°–81° | Venice turps | Tschirch and Weigel |
| β-Larinolic | $C_{18}H_{26}O_2$ | 85°–86° | ,, | ,, |
| α-Accracopalolic | $C_{18}H_{30}O_2$ | 152°–155° | Accra copal | |
| Loangocopalolic | $C_{18}H_{34}O_2$ | — | Loango copal | Tschirch and Willner |
| Abietic | $C_{19}H_{28}O_2$ or $C_{44}H_{64}O_5$ | 153°–154° | Colophony | Maley-Mach |
| Canadolic | $C_{19}H_{28}O_2$ | 143°–145° | Canada balsam | Tschirch |
| α-Canadinolic | $C_{19}H_{30}O_2$ | 88°–95° | ,, | ,, |
| β-Canadinolic | $C_{19}H_{30}O_2$ | 90°–95° | ,, | ,, |
| Congocopalic | $C_{19}H_{30}O_2$ | 115°–118° | Congo copal | Engel |
| Bengucopalic | $C_{19}H_{30}O_2$ | 134°–136° | Benguelo copal | ,, |
| β-Accracopalolic | $C_{19}H_{32}O_2$ | 144°–148° | — | — |
| Metairesinolic | $C_{19}H_{32}O_7 3H_2O$ | — | Matai (resin of Podocarpus spicatus) | Easterfield and Bec |
| Canadinic | $C_{19}H_{34}O_2$ | 135°–136° | Canada balsam | Tschirch |
| Guaiaretic | $C_{20}H_{21}O_4$ | 86° | Guaiacum | Döbner and Lücker |
| Guaiacic | $C_{20}H_{24}O_4$ | 75°–80° | ,, | ,, |
| Guaiaconic | $C_{20}H_{24}O_5$ | 95°–100° | ,, | Kerzig and Schiff |
| Abietolic | $C_{20}H_{28}O_2$ | 145°–153° | Strasburg turps | Tschirch |
| Illuric | $C_{20}H_{28}O_3$ | 128° | African copaiva | ,, |
| d-Pimaric | $C_{20}H_{30}O_2$ | 210°–211° | — | Vesterburg |
| l-Pimaric | $C_{20}H_{30}O_2$ | 140°–150° | Bordeaux turps | ,, |

## CONSTITUENTS OF RESINS AND BALSAMS

### Resinolic Acids (*continued*)—

| Name of Acid. | Formula. | Melting Point. | Source. | Observer. |
|---|---|---|---|---|
| *i*-Pimaric | $C_{20}H_{30}O_2$ | 171° | Bordeaux turps | Vesterburg |
| Laricinolic | $C_{20}H_{30}O_2$ | 147°–148° | Larch turps | Tschirch and Weigel |
| Sandaracopimaric | $C_{20}H_{30}O_2$ | 170° | Sandarac | Tschirch and Wolff |
| β-Benicopalolic | $C_{20}H_{30}O_2$ | 119° | Benin copal | Tschirch and Kahan |
| Picea-pimaric | $C_{20}H_{30}O_2$ | 144°–145° | Jura turps | — |
| α-Colophonic | $C_{20}H_{30}O_2$ | 177°–182° | Pine resin | Klason and Kohler |
| Sylvic | $C_{20}H_{30}O_2$ | — | — | — |
| β-Colophonic | $C_{20}H_{30}O_2$ | 168°–173° | Pine resin | Klason and Kohler |
| Abietic | $C_{20}H_{30}O_2$ | — | — | Fahrion |
| Palabietinic | $C_{20}H_{30}O_2$ | 153°–154° | Pinus palustris | Tschirch |
| Beljiabietinic | $C_{20}H_{30}O_2$ | — | Russian white pitch | ,, |
| Copaivic | $C_{20}H_{30}O_2$ | — | Copaiba balsam | Schweitzer |
| Para-copaivic | $C_{20}H_{32}O_3$ | 145°–148° | ,, ,, | Tschirch and Keto |
| α-Loangocopalic | $C_{20}H_{36}O_2$ | 134° | Loango copal | Tschirch and Willner |
| Guaiacic | $C_{21}H_{22}O_7$ | — | Guaiacum | Döbner and Lücker. |
| α-Benicopalinic | $C_{21}H_{30}O_3$ | 187° | Benin copal | Tschirch and Kahan |
| Bengucopalolic | $C_{21}H_{32}O_3$ | 114°–116° | Benguelo copal | Engel |
| Accracopalic | $C_{21}H_{34}O_3$ | 104°–106° | — | — |
| Cameroo-copalolic | $C_{21}H_{36}O_3$ | 98°–100° | Cameroon copal | Tschirch and Rackwitz |
| Leonecopalolic | $C_{21}H_{38}O_2$ | 133° about | Sierra Leone copal | Tschirch and Willner |
| Congocopalolic | $C_{22}H_{34}O$ | 108°–110° | Congo copal | Engel |
| Sandaracic | $C_{22}H_{34}O_3$ | 186°–188° | Sandarac | Tschirch and Wolff |
| Beetroot resin acid | $C_{22}H_{36}O_2 . H_2O$ | 299°–300° | Beetroot | Andelik and Votoček |
| α-Masticic | $C_{23}H_{36}O_4$ | 90°–91° | Mastic | Tschirch and Reutter |
| β-Masticic | $C_{23}H_{36}O_4$ | 89·5°–90·5° | ,, | ,, ,, |
| Masticolic | $C_{23}H_{36}O_4$ | 201° | ,, | ,, ,, |
| Ango-copalolic | $C_{23}H_{36}O_3$ | 85° | Angola copal | Tschirch and Rackwitz |
| Succino-sylvic | $C_{24}H_{36}O_2$ | — | — | — |
| Sandaracinolic | $C_{24}H_{36}O_3$ | 265°–275° | Sandarac | Tschirch and Wolff |
| Loangocopalinic | $C_{24}H_{44}O_2$ | 165° | — | Tschirch and Willner |
| Leonecopalic | $C_{24}H_{48}O_3$ | 142° about | Sierra Leone copal | ,, ,, |

| | | | | |
|---|---|---|---|---|
| α-Picea-pimarolic | $C_{25}H_{44}O_2$ | 90°–95° | Jura turps | Tschirch |
| β-Picea-pimarolic | $C_{25}H_{44}O_2$ | 88°–94° | ,, ,, | ,, — |
| Benicopalenic | $C_{27}H_{48}O_2$ | 101° | Benin copal | |
| Chironoiic | $C_{28}H_{48}O_4$ | 100°–108° | Burseraceous opoponax | Tschirch and Baur |
| Callitrolic | $C_{30}H_{48}O_5$ or $C_{65}H_{84}O_8$ | — | Sandarac | ,, ,, |
| Succino-abietic | $C_{32}H_{48}O_2$ or $C_{80}H_{120}O_5$ | 148° | Amber | Henry, Tschirch, and Belzer |
| α-Masticonic | $C_{32}H_{48}O_4$ | 96°–96·5° | Mastic | Tschirch and Reutter |
| β-Masticonic | $C_{32}H_{48}O_4$ | 91°–92° | ,, | |
| Boswellic | $C_{32}H_{52}O_4$ | 142°–150° | Olibanum | Tschirch and Halbey |
| α-Elemic | $C_{35}H_{46}O_4$ or $C_{37}H_{56}O_4$ | — | Elemi | Flückiger |
| Elemic | $C_{37}H_{56}O_4$ | 215° | ,, | Tschirch and Saal |
| Isoelemic | $C_{37}H_{56}O_4$ | 120° | ,, | ,, ,, |
| α-isotacelemic | $C_{37}H_{56}O_4$ | 120°–121° | ,, | ,, ,, |
| Tacelemic | $C_{37}H_{56}O_4$ | 215° | ,, | ,, ,, |
| β-isotacelemic | $C_{37}H_{56}O_4$ | 120° | ,, | ,, ,, |
| α-isocololemic | $C_{37}H_{56}O_4$ | 120°–122° | Colophonia elemi | ,, ,, |
| Coleleminic | $C_{37}H_{56}O_4$ | 215° | ,, ,, | ,, ,, |
| β-isocololemic | $C_{37}H_{56}O_4$ | — | Elemi | ,, ,, |
| Carelemic | $C_{37}H_{56}O_4$ | 120° | Carana elemi | ,, ,, |
| Caricelemic | $C_{37}H_{56}O_4$ | 120° | Caricari elemi | Tschirch and Reutter |
| Isocariceleminic | $C_{38}H_{56}O_4$ | 75°–76° | ,, ,, | ,, ,, |
| Cariceleminic | $C_{38}H_{56}O_4$ | 215° | ,, ,, | ,, ,, |
| Elemenic | $C_{39}H_{56}O_4$ | 215° | Elemi | Tschirch and Saal |
| Isoelemenic | $C_{39}H_{56}O_4$ | 75° | ,, | ,, ,, |
| Careleminic | $C_{40}H_{56}O_4$ | 215° | Carana Elemi | ,, ,, |
| Isocareleminic | $C_{40}H_{56}O_4$ | 75° | ,, ,, | ,, ,, |
| Tacamolic | $C_{43}H_{72}O_2$ | 95° | Tacamahac | ,, ,, |
| Elemic | $C_{44}H_{80}O_4$ | — | Elemi | ,, — |
| Trachylolic | $C_{56}H_{88}O_8$ | 165°–168° | Zanzibar copal | Tschirch and Stephan |
| Iso-trachylolic | $C_{56}H_{88}O_8$ | 105°–107° | ,, ,, | ,, ,, |
| Dammaroilc | $C_{56}H_{80}O_8$ | — | Dammar | Tschirch and Glimann |

of toluresinotannol (differing only by a surplus of $CH_2$), and xanthoresinotannol seems to be a homologue of erythroresinotannol, the difference amounting to 3 $CH_3$. Similarly, relationships exist between sagaresinotannol and xanthoresinotannol; and probably panaxresinotannol also belongs to the group with 18, or 17, carbon atoms. Finally, it can be seen that all the resinotannols contain only a single hydroxyl in the molecule. The readiness with which picric acid is formed when the resinotannols are treated with nitric acid, rather indicates that this HO is connected with a benzene nucleus and not with one of the side chains, *i. e.* is cyclostatic, not streptostatic. Picric acid is most readily formed from the tannols of acaroid resin, though all the others also yield the same product without difficulty. In the case of ammoresinotannol and sagaresinotannol, styphnic acid (trinitroresorcin) is obtained, whilst galbaresinotannol furnishes camphoric acid and camphoronic acid. When fused with potash, fatty acids appear, and in some cases protocatechuic acid, or resorcin, is formed. The resinotannols, therefore, also belong to the aromatic series.

4. The *resin acids* or *resinolic acids*, which chiefly occur in the free state in resins, are, so far as they have been investigated, all oxyacids, *i. e.* contain hydroxyl and carboxyl. Their composition is given on pp. 16–19.

Certain relations appear to exist among the resin acids. Thus the only difference between trachylolic acid, its isomers, and dammarolic acid is one of eight hydrogen atoms, so that the first named may be regarded as to some extent an orthohydrodammarolic acid; and sandaracolic acid can, on the basis of Maly's formula, be considered as a homodioxyabietic acid. That furthermore, succinoabietic acid is allied to abietic acid may also be presumed from a comparison of the formulæ. Again, the acids in guaiacum appear to be

related to one another and also to copaibic acid and pimaric acid.

In this long list of resin acids there are probably several that are identical; in any case there are quite a number exhibiting the same composition and very nearly the same melting points, the differences being shown only by other characters, notably is this the case with the series $C_{20}H_{30}O_2$. No doubt further research will result in a shortening of the list and the verification of the composition of many of the acids.

A noteworthy circumstance is the relatively great resistance offered by many resinolic acids to potash in a state of fusion, as also the fact that both abietic acid and succinoabietic acid furnish succinic acid when fused with potash.

5. The *resenes* undoubtedly form the most difficult class of the constituents of resins to deal with, and their resistance towards the majority of reagents renders their classification impossible for the present. They are neither hydrocarbons nor alcohols, acids, esters, ketones, nor aldehydes, but, so far as they have been examined, appear to belong to the aromatic series. They are all insoluble in potash. This resistance, however, is just the quality that places them for practical purposes among the most valuable constituents of the resins,[1] since the value of a resin in practice is so much the higher in proportion to its power of resisting manifold attacking influences. The following resenes are known (see pp. 22–23).

That the two panaxresenes are allied is seen by comparing their formulæ. The $\beta$-panaxresene is apparently an oxidation product of the $\alpha$-resene. The same applies to

[1] Hence we find the resins employed for varnish-making, *e. g.* copal, dammar, dragon's-blood, etc., contain relatively large amounts of resenes. Whether this is a predominant factor in determining their value, and a quantitative examination desirable, is a matter that would repay attention and prove of interest.

## RESENES

| Name. | Formula. | Melting Point. | Source. | Observer. |
|---|---|---|---|---|
| Myroxoresene | $C_{17}H_{10}O$ | — | Fruit of Myroxylon | Tschirch |
| Olibanoresene | $(C_{14}H_{22}O)n$ | 62° | Olibanum | Tschirch and Halbey |
| Tacaleresen | $(C_{15}H_{20}O)n$ | 75° | Tacamahaca elemi | Tschirch and Saal |
| β-Tacoresen | $C_{15}H_{25}O_2$ | 82° | Tacamahac | ,, ,, |
| Gurjunresene | $C_{17}H_{28}O_2$ | — | Gurjun balsam | Tschirch and Weil |
| Abietoresene | $C_{19}H_{30}O$ | 168°–169° | Strasburg turps | Tschirch and Weigel |
| Mancopalresene | $C_{20}H_{32}O$ | 80°–85° | Manila copal | Tschirch and Koch |
| Dracoalban | $C_{20}H_{40}O_4$ | — | Palm dragon's blood | Tschirch and K. Dietrich |
| α-Tacoresene | $C_{21}H_{32}O_2$ | 93°–95° | Tacamahac | Tschirch and Saal |
| Juroresene | $C_{21}H_{36}O$ | — | Jura turps | Tschirch |
| Canadoresene | $C_{21}H_{42}O$ | 170° | Canada balsam | Tschirch and Brunning |
| α-Bengucoloresene | — | — | Benguelo copal | — |
| β-Bengucoloresene | $C_{22}H_{36}O_2$ | 192°–196° | ,, ,, | Engel |
| Sandaracoresene | $C_{22}H_{36}O_2$ | 57° | Sandarac | Tschirch and Saal |
| Caricelresene | $C_{24}H_{46}O_2$ | 75°–76° | Caricari elemi | Tschirch and Reutter |
| α-Cameroo-copalresene | — | — | — | — |
| β-Cameroo-copalresene | $C_{25}H_{36}O_4$ | 220°–224° | Cameroon copal | Tschirch and Kotch |
| β-Angocopalresene | $C_{25}H_{38}O_4$ | 220°–224° | Angola copal | Tschirch and Rackwitz |
| α-Copalresene | $C_{25}H_{38}O_4$(?) | 75°–77° | Copal | Tschirch and Stephan |
| β-Copalresene | $C_{25}H_{38}O_4$ | — | ,, | ,, ,, |
| ψ-Euphorboresene | $C_{25}H_{64}O_{10}$ | 54°–55° | False euphorbium | Tschirch and Leuchtenberger |
| α-Congocopaloresene | — | 175°–178° | Congo copal | Engel |
| β-Congocopaloresene | — | — | ,, ,, | ,, |
| Heerabol-resene | $\{C_{26}H_{34}O^5$ or | — | — | — |
| | $\{C_{26}H_{31}O_2(OH)_3$ | — | — | — |

| | | | | |
|---|---|---|---|---|
| Dracoresene | $C_{26}H_{44}O_2$(?) | 74° | Palm dragon's blood | Tschirch and K. Dietrich |
| Caraleresene | $C_{27}H_{40}O_2$ | 75°–77° | Carana elemi | ,, and Saal |
| α-Euphorboresene | $C_{28}H_{48}O$ | 75° | Euphorbium | ,, and Paul |
| Bisabol-resene | $C_{29}H_{47}O_6$ | — | Russian white pitch | — |
| α-Angocopalresene | $C_{30}H_{54}O_6$ or $C_{30}H_{56}O_6$ | 63°–65° | Angola copal | Tschirch and Rackwisz |
| Beljoresene | $C_{31}H_{36}O$ | — | — | — |
| β-Damarresene | $C_{31}H_{52}O$ | 206° | Dammar | Tschirch and Glimann |
| β-Panaxresene | $C_{32}H_{52}O_5$ | — | Burseraceous opoponax | Tschirch and Baur |
| α-Panaxresene | $C_{32}H_{54}O_4$ | — | ,, ,, | ,, ,, |
| Euphorboresene | $C_{33}H_{48}O_4$ | 74°–76° | Euphorbium | Tschirch and Paul |
| α-Dammarresene | $C_{33}H_{52}O_3$(?) | 65° | Dammar | Tschirch and Glimann |
| α-Masticoresene | $C_{35}H_{56}O_4$ | 74°–75° | Mastic | Tschirch and Reutter |
| β-Masticoresene | $C_{35}H_{56}O_4$ | ,, | ,, | ,, ,, |
| α-Storesene | $C_{35}H_{35}(OH)_3$ | — | Oriental storax | — |
| β-Storesene | $C_{35}H_{35}(OH)_3$ | — | ,, ,, | — |
| Alban | $C_{40}H_{64}O_3$ | 195° | Gutta-percha | Tschirch and Oesterle |
| Fluavil | $C_{40}H_{64}O_4$(?) | — | ,, ,, | Tschirch and Osterle |
| Bordoresene | — | — | Bordeaux turps | — |
| Lariresene | — | — | Venice turps | — |
| Silvoresene | — | — | Finland turps | — |
| Paloresene | — | — | Pinus palustris | — |
| Heeraboresene | $C_{42}H_{56}O_9$ | 100°–102° | Heerabol myrrh | O. von Friedrichs |
| Honduresene | $C_{64}H_{64}O_{10}$ | 310°–315° | White Peru balsam | Thoms and Biltz |
| Juroresene | — | — | Jura turps | — |
| α-Loangocopalresene | — | — | Loango copal | Tschirch and Willner |
| β-Loangocopalresene | — | — | ,, ,, | ,, ,, |
| α-Leonecopalresene | — | — | Sierra Leone copal | ,, ,, |
| β-Leonecopalresene | — | — | ,, ,, | — |
| Colaleresene | — | 75°–77° | Colophonia elemi | Tschirch and Saal |

fluavil and alban, as also to the dammarresenes. Moreover, a close relationship probably exists between the panaxresenes and the dammarresenes, as also between fluavil and alban on the one hand, and $\alpha$-copalresene on the other.

The foregoing results point to a fairly general concordance in the composition of the drugs in question; and, compared with other groups, a complete retirement of esters and alcohols, whilst the resin acids and resenes, together with the gums, form the main constituents. Specially noteworthy is the approximation of the empirical formulæ of boswellic and chironolic acids, and still more so that of the $\alpha$- and $\beta$-panaxresenes.

A comparative Table (see pp. 22, 23) of the chief resinotannols has also been compiled by Tschirch.

Finally, mention may be made of an interesting tabulation by Halbey of the behaviour of the constituents of resins towards the cholesterin reactions, the results being all the more valuable from having been obtained with the *pure substances*, and not the crude mixtures; hence the colour reactions may be regarded as perfectly reliable. Recently also, K. Dieterich has recommended working with the isolated resin acids and alcohols in quantitative estimations, in the same way as that adopted for fats; since, just as certain reactions of oils and fats are characteristic for the corresponding pure constituents alone, so the investigation of the isolated constituents of resins may lead to better concordance in the resulting values. The cholesterin reactions are given in the subjoined tables (pp. 26–27).

On the basis of the oxidation, reduction, and fission products of the substances hitherto found in resins, and also of the potash-fusion test,[1] the resins and their con-

[1] See Wiesner and Hlasiwetz, *Die technisch verwertheten Balsame Harze, und Gummiharze*, 1869, pp. 70 *et seq.*, 81–84.

stituents may be regarded, almost without exception, as aromatic, and not aliphatic, derivatives.

Whereas nitrogenous bodies are rarely, if ever, found in the gum resins, balsams, and resins, sulphur compounds are more frequent, *e. g.* in asafœtida, succinite, and sagapenum. It is one of the main advances made in the modern chemistry of resins that substances formerly regarded as uniform have now been separated into several well-defined constituents. To these results—a valuable success attained by Tschirch and his pupils—we are indebted for a further advantage, viz. the possibility of more uniform nomenclature for the resins; the names introduced by Tschirch, such as resins, resinols, resinotannols, resinolic acids, resenes, etc., being now well known and adopted generally.

**Classification of Resins.**—According to the most recently published report by Tschirch (Paper read before the Naturforscherversammlung—Meeting of the German Association of Natural Philosophy—at Munich, 1899), the following classification of the resinous bodies has been drawn up :—

1. *Resinotannol resins*—
   - (*a*) Benzoic acid resins.
   - (*b*) Umbellifer resins.
2. *Resene resins*—
   - (*a*) Droseraceæ resins.
   - (*b*) Dipterocarpeæ resins.
3. *Resinol resins.*
4. *Resinol acid resins*—
   - (*a*) Coniferæ resins.
   - (*b*) Cæsalpinoideæ resins.
5. *Gluco resins.*

## Behaviour of Resin Constituents towards the Cholesterin Reactions.

| Substance. | Formula. | Analyst. | Melting Point. | Hesse's Reaction. | | Drop Coloration in the Porcelain Basin. | Liebermann's Reaction. |
|---|---|---|---|---|---|---|---|
| | | | | $CHCl_3$. | $H_2SO_4$. | | |
| **Substances imparting a deep Red coloration to Chloroform in Hesse's Test.** | | | | | | | |
| Cholesterin . . | $C_{26}H_{44}O+H_2O$ | Mauthner | 148·5° C. | blood red | pale yellow | blue, green, yellow | red, blue, green |
| Phytosterin (from grass leaves) . | $C_{26}H_{44}O+H_2O$ | Tschirch | 132°–133° | cherry red | pale yellow | blue, green, yellow | red, blue, green |
| Lanolin . . . | — | — | — | red-brown | yellow | blue, green, yellow | yellow, green |
| Myroxin . . . | $C_{23}H_{36}O$ | Tschirch and Germann | — | blood red | pale yellow | dirty green, yellow | faint reddish |
| Dracoalban . . | $C_{20}H_{10}O_4$ | Tschirch and K. Dieterich | — | red-brown | yellow | dirty green, yellow | red, brown-red |
| Olibanoresene . | $(C_{14}H_{22}O)n$ | Tschirch and Halbey | 62° | blood red | red | green, yellow | red, brownish green |
| Dracoresene . . | $C_{20}H_{44}O_2$ | Tschirch and K. Dieterich | 74° | dark red | red | dirty green, yellow | red, dark red, brown |
| α-Panaxresene . | $C_{32}H_{54}O_4$ | Tschirch and Baur | — | deep red | blood red | between yellow-brown and olive-green | brown-red, brown |
| **Substances of totally different behaviour in the Hesse Reaction.** | | | | | | | |
| Isocholesterin. . | $C_{26}H_{44}O$ | E. Schulze | 137°–138° | colourless, red later | pale yellow | — | red, yellow |
| Dammarresene . | α : $C_{11}H_{17}O$<br>β : $C_{31}H_{52}O$ | Tschirch and Glimmann | 65°<br>206° | red-yellow | pale yellow | indefinite | turbid rose red, then bluish |
| Chironol . . . | $C_{28}H_{48}O$ | Tschirch and Baur | 173°–176° | yellow, afterwards dirty violet | yellow, afterwards reddish yellow | faintly green | cherry red, violet |
| **Substances imparting a slight Red coloration with Chloroform in Hesse's Test.** | | | | | | | |
| Abietic acid . . | $C_{19}H_{28}O_2$ | Mauch | 165° | reddish yellow | blood red | absence of characteristic transitions | red, violet, brown, green |
| Euphorbon . . | $C_{20}H_{36}O$ | Henke | 113°–114° | reddish yellow | blood red | — | red, brownish green |
| Succinoabietol . | $C_{40}H_{60}O_2$ | Tschirch and Aweng | 124° | reddish yellow | blood red | — | red, brown |
| Storesinol . . . | $C_{16}H_{25}O_2$ | Tschirch and van Itallie | — | reddish yellow | blood red | ill-defined | violet, bluish green, green |
| Myroxoresene . . | $C_7H_{10}O$ | Tschirch and Germann | — | reddish yellow | brownish red | brownish | brown-red |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| α-Copalresene | $C_{41}H_{68}O_4$ | Tschirch and Stephan | 75–77° | reddish yellow, | red | brownish yellow | brown |
| Benzoresinol | $C_{16}H_{28}O_2$ | Tschirch and Lüdy | 274° unc. | yellow, afterwards reddish yellow | blood red | ill-defined | cherry red, red-brown |
| Dammarolic acid | $C_{56}H_{80}O_8$ | Tschirch and Glimmann | — | yellow, afterwards reddish yellow | red | — | red, dark red |

**Substances producing merely Yellow or no coloration with Chloroform in Hesse's Reaction.**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Succinoabietic acid | $C_{80}H_{120}O_5$ | Tschirch and Aweng | 148° | yellow | red | ill-defined | reddish brown |
| Sandaracolic acid | $C_{45}H_{66}O_7$ | Tschirch and Balzer | 140° (152°) | yellow | red | — | reddish brown |
| Boswellic acid | $C_{32}H_{52}O_4$ | Tschirch and Halbey | 142°–150° | yellow | blood red | — | red, dark brown-red |
| Chironolic acid | $C_{28}H_{48}O_4$ | Tschirch and Baur | 100°–108° | yellow | red | — | red |
| Trachylolic acid | $C_{56}H_{88}O_8$ | Tschirch and Stephan | 165° | yellow | red | — | red-brown, dirty brown |
| Callitrolic acid | $C_{65}H_{84}O_8$ | Tschirch and Balzer | 248° | yellow | blood red | — | red, red-brown |
| Copaibic acid | $C_{20}H_{30}O_2$ | H. Rose | — | yellow | red | — | red, red-brown |
| β-Panaxresene | $C_{32}H_{52}O_5$ | Tschirch and Baur | — | yellow | blood red | — | red-brown |
| Isotrachylolic acid | $C_{56}H_{88}O_8$ | Tschirch and Stephan | 105°–107° | yellow | dark red | brown-yellow | brown |
| β-Copalresene | $C_{25}H_{38}O_4$ | Tschirch and Stephan | — | yellow | red-yellow | brown-yellow | brown |
| Guaiaconic acid | $C_{20}H_{24}O_5$ | Döbner and Lücker | 95°–100° | pale yellow | dark violet | yellow, blue-green, green | dark violet |
| Pinoresinol | $C_{18}H_{18}O_6$ | Bamberger | 80°–90° | colourless | red, red-violet | — | red, brown-red |
| Lariciresinol | $C_{16}H_{18}O_5$ | Bamberger | 164° | colourless | rose red | — | rose red |
| Myroxol | $C_{46}H_{68}O_{10}$ | Tschirch and Germann | — | colourless | dark red | yellow | brown |
| Guaiacic acid | $C_{20}H_{24}O_4$ | Döbner and Lücker | 75°–80° | colourless | rose red | — | rose red |
| Succinoresinol | $C_{12}H_{20}O$ | Tschirch and Aweng | 275° | pale yellow | reddish yellow | — | dirty brown |
| Myroxocerin | $C_{12}H_{20}O$ | Tschirch and Germann | 95° | yellow | yellow | yellowish | faintly reddish |
| Alban | $C_{40}H_{64}O_2$ | Tschirch and Oesterle | 195° unc. | pale yellow | yellow | — | red, brown-red |
| Agaric acid | $C_{16}H_{30}O_5+H_2O$ | Jahns | 138°–139° | colourless | yellow | — | yellow |
| Podocarpic acid | $C_{17}H_{22}O_3$ | Oudemans | 187/8° | colourless | yellow | — | purple-red, yellow-green |
| Aleuritic acid | $(C_{13}H_{26}O_4)n$ | Tschirch and Farner | 101·5° | colourless | slightly yellow | — | slightly yellow |
| Myroxofluorin | $C_{42}H_{64}O_{10}$ | Tschirch and Germann | — | colourless | yellow green | bluish, colourless | pale yellow, dark yellow |

**Uses of Resins.**—These substances are widely utilised for technical, medicinal, and pharmaceutical purposes. Colophony, elemi, dammar, mastic, copal, amber, sandarach, and other light-coloured resins are more particularly employed in the preparation of varnishes, though some of them, *e. g.* copal, dammar, and amber, have to undergo certain preparatory treatments, such as distillation, fusion, etc., in order to convert the hard and comparatively insoluble resins into soluble products. The copal varnishes are the most highly esteemed of any. Colophony and acaroid resins are used for sizing paper, and are also distilled for the production of gas and resin oil, colophony, in particular, being very largely employed for this purpose. For pharmaceutico-medicinal uses—preparation of plasters, ointments, etc.—the balsams, storax, turpentine, colophony, and gallipot are utilised; and copaiba and Peruvian balsam belong to the category of highly efficacious medicaments. The turpentines in particular are worked up into a large number of primary and secondary substances, and furnish oil of turpentine, colophony, various kinds of pitch, resin oils, resina pini, etc. The gummy substances left behind in the treatment of gum resins are used as agglutinants. Taken collectively, the employment of resinous substances has been exceedingly varied and extensive from time immemorial.

**Identification of Resins; Qualitative and Colour Reactions.**—At first, qualitative methods alone were employed in the analysis and identification of resins. The colour reactions, in particular, were very numerous, some of these being still employed in the absence of better methods. So great was the complexity of these various reactions, and so conflicting the results obtained therewith, that it must be a source of gratification to know modern attempts at establishing quantitative methods have in many cases

displaced them. The most important colour reactions of a general character are those of Storch-Morawski, Ellram (vanillin-sulphuric acid), and above all, the cholesterin reactions already described as due to Tschirch and his pupils. Mauch's proposal to apply the colour reactions to the oils isolated by means of chloral hydrate must also be considered a progressive step. Numerous special colour reactions, etc., are due to Hirschsohn; and, as in the case of fats and oils, the fatty acids are now considered the fittest subjects for the colour reactions, so Tschirch, by determining the cholesterin reactions of the resinotannols and the resinols, and K. Dieterich, by employing the resin alcohols and resin acids as the basis of quantitative and qualitative analysis, have brought the examination of the resinous substances more into conformity with that of the fats and oils, and therefore into a more reliable path than hitherto.

As already mentioned, and as will be shown again later, the future of resin analysis, as in the case of the fats and oils, lies in the selection of quantitative methods in preference to qualitative and colour reactions.

**Identification and General Reference to Quantitative Methods of Testing.**—The quantitative analysis of resins is divided into two branches—(1) quantitative identification; and (2) actual quantitative investigation for purity. Although the identity of a resin can in most cases be determined by the external and physical characteristics, confirmed by its chemical behaviour and the above-mentioned qualitative reactions, there are also certain quantitative constants, such as the acid, ester, and saponification values, which afford information, not only as to whether the product is really the resin it is supposed to be, but also whether it is free from extraneous admixtures.

**Melting point, Specific Gravity, Ash, Moisture,**

**Special Determinations.**—Further quantitative estimations that may be performed are: the conditions of solubility, melting point, specific gravity, percentage of ash and moisture, and such special determinations as testing for cinnamein in Peruvian balsam, the carbonyl, methoxyl, acetyl values, and the investigation of the resin acids and resin alcohols.

**Solvents.**—The principal quantitative methods of testing for purity are not such as are applicable to merely subordinate constituents of the resins—*e. g.* the carbonyl value—but those referring to the main constituents. To this class belong the acid and saponification values, and the quantitative determination of the portions extractable by various solvents—alcohol, ether, etc., and, more recently, chloral hydrate (Mauch [1])—as formerly practised by Guichard, Hirschsohn, Kremel, E. Dieterich, etc., and continued by K. Dieterich.

An interesting precursor of chloral hydrate for this purpose was sodium salicylate, which, according to Conrady, is capable of partially or entirely dissolving numerous resins and gum resins. Flemming's method of dissolving copal and amber in epi- and di-chlorhydrin is also worthy of mention; the following table showing the results of Valenta's application of the last two solvents to a large number of resins:—

| Resin. | Epichlorhydrin. | Dichlorhydrin. |
|---|---|---|
| Elemi. | Readily and completely soluble, both in the cold and on heating, forming yellow to greenish solutions, which leave a clear, sticky residual layer on evaporation. | Readily and completely soluble. The solution turns brown when heated. |

[1] Dissertation, Strasburg, 1899.

| Resin. | Epichlorhydrin. | Dichlorhydrin. |
|---|---|---|
| Mastic. | Readily soluble in either cold or warm. Solution pale yellow, leaving a lustrous, colourless layer on evaporation. | Less readily soluble. The solution turns brown when heated. |
| Dammar. | Imperfectly soluble; more readily so hot. The clear yellowish filtrate gives a solid, clear, colourless layer of varnish. | Dissolves fairly readily to a brown solution in the cold. When heated, the colour turns to deep brown-violet. |
| Courbaril copal. | Imperfectly soluble in the cold, almost entirely so on heating, to a clear yellowish varnish. | Perfectly soluble in the cold to a yellow solution, which turns brown when heated. |
| Dragon's-blood. | Readily soluble, except for a brown residue. The solution is blood red, but gives a clear layer of varnish. | Imperfectly and less readily soluble; solution yellowish red in colour. |
| Sandarach. | Imperfectly soluble in the cold or hot. Solution pale yellow. | Dissolves perfectly in the cold to a brownish yellow solution, becoming deep brown when heated. |
| Bleached shellac. | Sparingly soluble; imperfectly so even when hot. | Readily and perfectly soluble on heating. Solution yellowish, does not turn brown; varnish layer dries very slowly. |
| Zanzibar copal. | Partially soluble in the cold, more readily on heating. Solution light yellow in colour, and gives a hard, clear stratum. | Partially soluble in the cold to a brownish solution, turning dark brown when heated. |
| Angola copal. | Partially soluble in the cold, more readily hot. The faint yellow solution gives a solid varnish layer. | More readily soluble. Solution turns brown when heated. |

| Resin. | Epichlorhydrin. | Dichlorhydrin. |
|---|---|---|
| Manila copal. | Partially soluble in the cold (the insoluble portion swelling up to a gelatinous mass), almost completely so by heat. Gives a yellow solution, and solid varnish layer. | The greater part soluble in the cold. The brownish yellow solution turns brown when heated. |
| Kauri copal. | Partially soluble in the cold (the remainder swelling up), perfectly so when hot. Colour pale yellow; varnish clear. | Almost perfectly soluble to brownish yellow solution, which turns brown when heated. |
| Amber. | Partially and very slowly soluble. Solution yellow. | Sparingly soluble. The lumps of amber turn brown when heated. |
| Asphaltum. | Very sparingly soluble, cold or hot. | Very sparingly soluble, cold or hot. |

The solubility of resins in terpineol and in carbon tetrachloride is given in the following Table :—

| | Terpineol. | | Carbon Tetrachloride. | |
|---|---|---|---|---|
| | Cold. | Hot. | Cold. | Hot. |
| Colophony . . | Soluble | Soluble | Partly soluble | Soluble |
| Sandarac . . . | Insoluble | Soluble | Insoluble | Insoluble |
| Amber . . . . | Insoluble | Insoluble | Insoluble | Insoluble |
| Asphaltum . . | Partly soluble | Soluble | Soluble | Soluble |
| Elemi . . . . | Insoluble | Soluble | Almost all dissolved | Soluble |
| Mastic . . . . | Soluble | Soluble | Partly dissolved | Partly dissolved |
| Manila copal . . | Insoluble | Partly soluble | Softened | Softened |
| Benzoin . . . | Insoluble | Soluble | Insoluble | Partly soluble |
| Copal . . . . | Softened | Softened | Insoluble | Partly soluble |
| Kauri . . . . | Softened | Softened | Softened | Soluble |
| Dammar . . . | Dissolved | Dissolved | — | — |
| Shellac . . . | Insoluble | Soluble | Insoluble | Insoluble |

C. Coffignier found that terpineol dissolved kauri, pontianac, and hard manila completely, and that hard and semi-hard copals, such as Madagascar, Zanzibar, and Demerara, were not easily acted upon, even when heated, but formed thick solutions containing more or less swollen particles of undissolved resin.

These experiments are interesting in connection with the fact that M. Tixier and M. Ramband have taken out patents for the use of terpineol for dissolving resins in varnish manufacture.

A few experiments have been tried by the reviser with isoprene. This dissolved African copal in the cold to form a clear jelly, it also dissolved colophony in the same way. Dammar formed a translucent jelly. Sandarac, orange shellac, and kauri were scarcely affected by it.

The solubility of resins in essential oils is also given below :—

| 100 parts by weight of the following essential oils dissolve :— | Amber. | Rosin. | Copal. | Dammar. | Mastic. | Shellac. |
|---|---|---|---|---|---|---|
| Cajeput | 6·53 | 43·70 | 5·52 | 42·49 | 41·16 | 0·66 |
| Copaiba | — | 24·95 | 0 | 34·57 | — | — |
| Light camphor oil | 9·73 | 46·16 | 9·16 | 34·95 | 35·04 | 1·33 |
| Heavy camphor oil | 6·50 | 31·35 | 2·81 | 50·08 | 37·98 | 0·83 |
| Lavender | — | 52·86 | — | 33·07 | — | — |
| Cloves | — | 79·79 | 0 | 18·27 | — | — |
| Rosemary | 10·16 | 48·94 | 4·81 | 99·44 | 21·39 | 0·79 |
| Alspice | 8·90 | 40·98 | 9·51 | 41·66 | 33·47 | 3·67 |
| Turpentine | 7·47 | 51·84 | — | 64·28 | 52·79 | 12·94 |
| Turpentine, rectified | 10·30 | — | 6·47 | — | — | — |
| Paraffin oil | — | — | — | 9·27 | — | — |
| Wax oil | 2·87 | — | — | 67·31 | — | — |

The following Table from the *Chemiker Zeitung* is due to Prof. Bottler :—

| Copals. | Alpha-di-chlorhydrin. | Methyl-ethyl ketone. | Terpineol. | Carbon tetrachloride. | Chloral hydrate solution. | Ether followed by alcohol. | Mixture of equal parts $CS_2$ & $C_6H_6$. | Acetone. |
|---|---|---|---|---|---|---|---|---|
| White Angola . | About 25 p.c. dissolved | About 10 p.c. dissolved | Mostly dissolved, but with a gelatinous residue | Insoluble | — | Soluble to turbid liquid | Almost entirely soluble | Soluble to turbid liquid |
| Red Angola . | About 10 p.c. dissolved | About 15 p.c. dissolved | ,, | ,, | Almost insoluble (80 p.c.) | ,, | Gelatinous without dissolving | — |
| White Benguela | About 10 p.c. dissolved | About 15 p.c. dissolved | ,, | ,, | Barely soluble (15 p.c.) | Partly soluble | Barely soluble | Soluble |
| Yellow Benguela | Almost insoluble | About 20 p.c. dissolved | ,, | ,, | Barely soluble (16⅔ p.c.) | ,, | Gelatinises without dissolving | Mostly soluble |
| Congo . . . | Partly dissolved | About 10 p.c. dissolved | ,, | ,, | Barely soluble (20 p.c.) | Slightly soluble | Almost entirely soluble | — |
| Sierra Leone . | ,, | About 50 p.c. dissolved | ,, | Almost insoluble | — | About 50 p. c. dissolved | Barely soluble | — |
| Cameroon . . | ,, | About 10 p.c. dissolved | Gelatinous without dissolving | About 25 p.c. dissolved | — | — | — | — |
| Zanzibar . . | Almost insoluble | About 10 p.c. dissolved | Mostly dissolved, but with a gelatinous residue | About 10 p.c. dissolved | — | Soluble mostly after long digestion | Barely soluble | Partly soluble |
| Brazil . . . | Completely soluble | Completely soluble | Completely soluble | Almost entirely soluble | Barely soluble (30 p.c.) | — | — | — |
| West Indies . | Almost insoluble | About 30 p.c. dissolved | Mostly dissolved, but with a gelatinous residue | About 10 p.c. dissolved | — | — | — | — |
| Kauri . . . | Completely soluble | Completely soluble | Completely soluble | ,, | Partly soluble (80 & 90 p.c.) | Almost entirely soluble | Gelatinises | Slightly soluble |
| Manila . . . | ,, | Almost entirely soluble | ,, | Insoluble | Mostly soluble (80 & 90 p.c.) | Entirely soluble | Mostly soluble | Gelatinises, a little dissolves |

The figures in brackets under chloral hydrate refer to the strength of the solution.

The action of chlorinated derivatives has recently been investigated by C. Coffignier, who found for copals the following amounts to be soluble :—

COPALS.

| | Zanzibar. | Madagascar. | Demerara. |
|---|---|---|---|
| Ethylene dichloride . . | 21·3 per cent. | 30·0 per cent. | 29·5 per cent. |
| ,, trichloride . . | 16·8 ,, | 29·2 ,, | 20·8 ,, |
| ,, perchloride . | 29·8 ,, | 11·8 ,, | 35·8 ,, |
| Tetrachlorethane . . . | 33·5 ,, | 62·2 ,, | 51·3 ,, |
| Pentachlorethane . . | 21·2 ,, | 37·0 ,, | 46·9 ,, |

He expresses the opinion that tetrachlorethane could be used to distinguish Zanzibar copal from the other two varieties.

Thomas H. Durrans has determined the solubility of various resins in pure amyl acetate and obtained the following results :—

| | Amount soluble in Amyl acetate. | | Amount soluble in Amyl acetate. |
|---|---|---|---|
| Colophony . . . . | 100 | Sierra Leone copal . | 75 |
| Damar . . . . . | 99 | Congo copal . . . | 68 |
| Hard Borneo copal . | 99 | Bombay glossy animi | 67 |
| New Zealand kauri . | 98 | Olibanum . . . . | 66 |
| Pontianac copal . . | 98 | Sandarach . . . . | 62 |
| Mastic tears . . . | 98 | Zanzibar animi . . | 61 |
| Hard copal I. . . . | 95 | Distilled copal . . . | 58 |
| ,, ,, II. . . . | 83 | Pure button shellac . | 48 |
| Kauri copal . . . | 82 | | |

The following solubilities of copals are given by C. Coffignier :—

| | Ethyl Alcohol. | Ether. | Amyl Alcohol. | Spirits of Turpentine. | Carbon Tetra-chloride. |
|---|---|---|---|---|---|
| Zanzibar | 14·10 | 25·00 | 36·70 | Insoluble | Insoluble |
| Madagascar | 26·20 | 35·00 | 77·60 | 39·70 | 15·00 |
| Demerara | 27·90 | 44·60 | 47·00 | 7·50 | 24·50 |
| Congo | 74·70 | 51·70 | 97·80 | 31·80 | 30·90 |
| Sierra Leone | 37·70 | 52·20 | 95·20 | 28·60 | 29·10 |
| Brazil | 69·80 | 70·30 | 98·20 | 51·80 | 55·10 |
| Benguela | 83·50 | 56·30 | 99·10 | 31·20 | 26·00 |
| Kissel | 42·60 | 57·40 | 91·50 | 20·40 | 30·10 |
| Kamerun | 33·30 | 44·20 | 70·80 | 21·40 | 26·30 |
| Accra | 52·20 | 56·00 | 95·90 | 20·30 | 19·70 |
| Kauri, blond | 93·40 | 38·20 | Soluble | 22·50 | 18·90 |
| ,, brown | 64·20 | 39·30 | Soluble | 26·40 | 22·70 |
| ,, busch | 87·70 | 52·70 | Soluble | 27·10 | 28·10 |
| Manila, hard | 44·10 | 41·50 | Soluble | 26·80 | 31·00 |
| ,, friable | Soluble | 71·30 | Soluble | 35·90 | 38·00 |
| Pontianac | Soluble | 54·00 | Soluble | 33·60 | 38·09 |
| Blue Angola | 84·90 | 72·70 | 98·60 | 30·60 | 38·70 |
| Red Angola | 62·40 | 48·70 | 93·00 | 23·00 | 22·30 |
| Colombia | 83·00 | 50·00 | 95·10 | 31·30 | 30·40 |

With regard to the solubility of resinous substances, it may be remarked that a certain amount of error may be introduced into the quantitative determination of the soluble portions by the absorption of oxygen during drying, special attention to which has been drawn by Weger's researches on the oxygen absorption of resins. Furthermore, it should be remembered, in case of conflicting reports, that the age of the resin and the time it has lain on the ground or covered up in the soil (*e. g.* dammar and sandarach) exercise great influence on its solubility. When quite fresh, both dammar and sandarach, also recent fossil resins, are more readily soluble than after a long sojourn in the place of discovery. Thoroughly fossilised resins, like the true copals, are, in consequence of their age, either soluble with great difficulty or almost entirely insoluble.

Sack gives the following particulars with regard to the solubility of the resins. His results, however, do not corre-

spond in more than an approximate manner with present-day experience :—

*Alcohol* readily dissolves colophony, shellac, sandarach, and mastic, whereas elemi is only sparingly soluble, copal cakes together, and dammar and amber are totally insoluble in this solvent.

*Ether* readily dissolves dammar, colophony, elemi, sandarach, and mastic; copal swells up; and amber and shellac remain undissolved.

*Acetic acid* has no action on any of the resinous substances except colophony, which swells up.

*Caustic soda* readily dissolves shellac, but colophony is only sparingly soluble, and the others not at all.

*Carbon di-sulphide* readily dissolves dammar and colophony; elemi, sandarach, and mastic with difficulty; copal swells up; while shellac and amber remain insoluble.

*Oil of turpentine* is a very good solvent for mastic, and a fair one of dammar, colophony, elemi, and sandarach, but does not dissolve shellac or amber, and merely causes copal to swell up.

*Benzol* dissolves dammar, colophony, and mastic very well, but is a poor solvent for elemi and sandarach, and does not dissolve amber or shellac.

*Petroleum ether* dissolves only dammar and mastic readily, colophony, elemi, and sandarach with difficulty, and the others not at all.

*Boiling linseed oil* has no solvent action on copal or amber, dissolves shellac, elemi, and sandarach with difficulty, but readily takes up dammar, colophony, and mastic.

*Ammonia* dissolves none of the resins but colophony, the latter with ease.

*Concentrated sulphuric acid* dissolves all the resins to

brown solutions, except dammar, which furnishes a bright red liquid.

The solubility of the resins in carbon di-sulphide formed the subject of special study by Guichard.[1]

**Acid Value.**—This constant (for definition, see Introduction to Part II.), which is useful in the quantitative analysis of resins, was at first determined by dissolving the resin or balsam in alcohol and titrating the solution with alkali direct, in a manner analogous to the method for fats; in the case of gum resins it was customary to make an alcoholic extract, generally, as stated in the Preface, in a very questionable manner. Since, with very many resins, especially where alcoholic extracts were used, the high coloration of the liquid rendered the titration very inaccurate, attempts have recently been made by K. Dieterich to obtain, by back titration, a liquid better suited for the purpose in view. In this method the alkali serves both to neutralise the acid, and to act as a solvent. Moreover, it presents the advantage, especially in the case of ester-free resins like copal, sandarach, dammar, etc., that all the resin acids are quantitatively combined. That this is not always the case with direct titration is shown by the results, which sometimes come out too low, and at other times are exceedingly variable.

Again, in the case of a number of resins which, like olibanum and asafœtida, which are difficult to saponify by the cold process, the acid value can be determined by back titration, although they contain esters. In such cases the mixture may be left for twenty-four hours without fear of saponification occurring, the esters present being very slow to saponify, at least in the cold. On the other hand, though with the various kinds of benzoin the acid value should be determined by back titration, the mixture should not be

[1] *A. d. Ph.* 205, p. 537; 207, p. 565.

left for more than five minutes, or saponification may ensue. The great advantage of back titration with all these resins is that, unlike the direct method, no solution has to be prepared, and no extracts or dark coloured liquids difficult of titration are obtained, but instead fairly pale, alkaline solutions of resin, easy to titrate, thus furnishing a clearer end reaction from red to white or yellow, than the change from brownish yellow to red given as in the direct method. Furthermore, Dieterich has elaborated a steam distillation process, analogous to the Reichert-Meissl method applied to fats, for driving off the volatile portions of such resins as are rich in ethereal oils and similar constituents (*e. g.* ammoniacum, galbanum, etc.). This method is, however, somewhat cumbrous, requiring considerable practice in its performance; but the author has also worked out a simpler process for ammoniacum and galbanum, consisting in the back titration of an aqueous alcoholic extract, so that the above determination of the volatile matters need not be performed except in doubtful cases. The main reason for employing back titration here is the one already given, namely, that the change from red to yellow on reaching the end-point is much sharper than that from yellowish brown to brown-red or red in direct titration. It may also be mentioned that the commercial grades of ammoniacum and galbanum have greatly deteriorated of late years, so that the values given by Dieterich as normal for the volatile matters in these substances can no longer be taken to apply to the ordinary present commercial qualities, but must be lowered.

The acid-value determination of myrrh, etc., is performed in a somewhat different manner, back titration being impracticable owing to incipient saponification. Most of the gum resins, being only partially soluble in alkali, require to be previously extracted by boiling with water and alcohol

(each a quarter of an hour in succession) under a reflux condenser. J. Marcusson and G. Winterfeld suggest the use of a mixture of equal parts of absolute alcohol and benzene as a solvent in the estimation of the acid value, several of the resins being completely soluble in this solution.

**Saponification Value.**—In determining the saponification value, the hydrolysis was formerly usually effected by a longer or shorter boiling with stronger or weaker caustic potash,—after the manner of the Köettstoefer method for fats. Sometimes an extract, at others the crude resin, was employed, the values in any event being subject to great fluctuation by reason of the lack of uniformity in the method of performance. Thus, Mills allowed the saponification to proceed for eighteen hours in a closed flask; Williams boiled for half an hour under a reflux condenser; Kremel, von Schmidt, Erban, Beckurts, and Brüche followed the same plan, but for the most part employed extracts from the drugs examined; while E. Dieterich also pursued the same course, but usually concentrated the mixture until the alcohol was expelled, and then took up the residue again with water and alcohol. In consequence of this variability, K. Dieterich attempted an improvement consisting in employing for each kind of resin the special method of saponification found most suitable to the case. Thus a trial—yielding only negatively useful results—was made with Tschirch's saponification method by passing hot steam through the alkaline liquid. Unfortunately none but very irregular decomposition values could in this way be obtained, the method proving unsuitable for analytical purposes, although well adapted for saponification on a large scale. After further experiments, Dieterich succeeded in devising two saponification methods for the various resinous substances, on lines precluding decomposition values, ensuring

perfect saponification, and at the same time furnishing liquids highly suitable for titration. These methods are the "cold" and "fractional" saponification tests.

**Cold and Fractional Saponification.**—Of these methods the first named has been more particularly tried on resins, whilst the fractional method is more suitable to the gum resins, the latter containing substances accessible to the action of alcoholic alkali on the one hand and aqueous alkali on the other. These methods have proved applicable to a number of resins, the main advantage being that perfect saponification can be secured with the natural drugs without the necessity of preparing extracts or solutions of the whole or a portion beforehand. Whilst in the cold saponification method the resin is simply left exposed to the action of benzine (sp. gr. 0·700) and alcoholic potash for twenty-four hours at room temperature, the fractional method entails a preliminary saponification with alcoholic alkali alone. A second saponification follows, which, just as the first was left for twenty-four hours in contact with the alcoholic alkali, is continued for twenty-four hours with aqueous alkali. The higher final values show that the gummy constituents of the gum resins are not completely acted upon before the final aqueous treatment.

**Resin Value; Total Saponification Value; Gum Value.**—The term "resin value" is applied by the author to the result of the simple alcoholic saponification + benzine, the result of the method employing alcoholic + aqueous alkali + benzine being named "total saponification value," whilst the difference between the two is the "gum value." (An explanation of these terms is given in the Introduction to Part II., p. 72.)

Since the saponification proceeds in definite stages, and certain constituents of the resins and gum resins are

saponified separately, the name " fractional saponification " is regarded as *à propos*. Certain resins, etc., which do not lend themselves to either of these cold processes, have still to be saponified by the hot method, under a reflux cooler and according to definite conditions. Special reference will be made at the conclusion of this section to the resins that can be saponified without recourse to heat. For the resinous products which have not yet been allotted any special method of saponification, the sole plan that can be accepted as uniform and suitable is that of saponification for half an hour under a reflux condenser, and back titration after cooling, *i. e.* the method adopted by Hübl for fats.

**Ester, Ether, and Anhydride Values.**—When the acid and saponification values are determined in separate experiments, the ester or ether values are found by subtracting the acid value from the saponification value. Where the ester value is ascertained in the same experiment as, and subsequent to, the acid value, by neutralisation followed by a further addition of alkali and saponification by one of the aforesaid methods, the saponification value is obtained indirectly, by adding together the acid and ester values. The term " ester value " is used in all, or at least in the principal, works on the subject (such as those of Kremel, Williams, Beckurts and Brüche, E. Dieterich, K. Dieterich, etc.), and not " ether value." Consequently the former term is correct for these values and for the esteriferous resins, even though synonymous with " ether value " and obtained by the same means. The " anhydride value " which expresses the amounts of true inner anhydrides, lactones, ester-anhydrides, and alcohol-anhydrides is not—as proposed by Benedikt—to be confounded with the ether and ester values. Benedikt also—in a manner decidedly open to objection—altered to " ether values " the values previously designated

" ester values " by Kremel, von Schmidt, and Erban. The author prefers to style all these values " ester values," since the true ethers, which would justify the term " ether value," have so far not been found in any of the resins except colophony.

**Constant Ether Value.**—In the case of colophony which was first shown by K. Dieterich to be devoid of esters, but which, according to Henriques, contains ethers and lactones, it has been proposed by the last-named worker to apply the term " constant ether value " to the values referring to these constituents. In any event the term " ether value " is more applicable to colophony than " ester value " would be, in the absence of any esters at all in that substance; and, moreover, as at present esters alone are known to exist in all other resins, it follows that the term " ester value " should be confined to resins containing esters. It should be mentioned that the ester and saponification values of resins often express other and secondary reactions, not merely the phenomenon of hydrolysis alone, and that these constants must be regarded more as empirical than as theoretical and scientifically accurate values.

For the further characterisation of the resins numerous methods have latterly been proposed, most of which are tedious and based on subsidiary constituents of the resins, nor have they sufficient practical importance to entitle them to mention, except as a matter of theoretical interest. These comprise the acetyl (HO group) value method for resins (K. Dieterich), the carbonyl value method (CO and COH groups) by Kitt, the methoxyl value method ($OCH_3$ groups) by Gregor, and the methods of examining the resin acids and resin alcohols proposed by K. Dieterich. (The definition of these different values will be found in the Introduction to Part II.)

**Acetyl Value ; Carbonyl Value ; Methoxyl Value.**—In the method proposed by K. Dieterich [1] for determining the *acetyl value* of resins, the substance is boiled under a reflux condenser, with an excess of acetic anhydride and a little anhydrous sodium acetate, until completely dissolved, or until it is evident that no further portion will pass into solution. The solution is poured into water, and the precipitate then ensuing is collected and extracted with boiling water until perfectly free from all traces of uncombined acetic acid. The insoluble residues left by copal and dammar are also treated in the same manner. The dried acetylised products are then tested for the acetyl, acid, ester, and saponification values by dissolving 1 grm. in cold alcohol and titrating with $\frac{1}{2}$ normal caustic potash. The saponification is also effected with $\frac{1}{2}$–n alkali for half an hour under a reflux condenser, and the product titrated back after cooling and dilution with alcohol (not water). As in the case of fats, the difference between the acetyl-saponification value and the acetyl-acid value gives the true "acetyl value."

Kitt's "**Carbonyl Value**" : [2]—The substance under examination is warmed with sodium acetate and an accurately measured quantity of phenylhydrazine chloride in dilute alcoholic solution. The excess of hydrazine salt not entering into the reaction is then ascertained by eliminating the nitrogen by oxidation with Fehling's solution and collecting the gas in a measuring tube. The carbonyl value, *i. e.* the percentage of carbonyl oxygen in the substance taken, is ascertained by the formula $O = V - VO \frac{0{,}07173}{S}$, wherein V — Vo indicates the difference in the volume of nitrogen reduced to O or 760 mm., and S refers to the weight of the substance in grms.

[1] *H. A.*, 1897, pp. 39–45. [2] *Ch. Ztg.*, 1898, p. 358.

The Gregor-Bamberger "**Methoxyl Value**" (Zeisel):[1] —As this method entails the use of apparatus and special precautions, it is considered preferable to repeat the author's own description in full.

The Zeisel apparatus is made up as follows:—A reflux condenser, fed with water at 40°–50° C., is fitted with a small flask, the neck of which is provided with a lateral tube for the introduction of carbon dioxide. The upper end of the condenser tube is connected with a Geissler potash apparatus which is charged with amorphous phosphorus suspended in water, and is placed in a water bath kept at about 50°–60° C., its purpose being to free the current of alkyl-iodide vapour passing through from hydriodic acid and iodine vapour. The alkyl iodide is led into a 4 per cent. solution of silver nitrate in two successive flasks, the whole being generally retained and converted into silver iodide in the first one. In performing the experiment, the substance to be examined for methoxyl is heated along with 10 c.c. of hydriodic acid of sp. gr. 1·68, $CO_2$ being passed through the apparatus. The experiment is complete when the liquid in the first flask has become clear above the deposit of silver iodide, and the silver iodide is then determined by gravimetric means.

Since the publication of this method by Zeisel, the improvements made have been insignificant; Herzig[2] proposed to add acetic anhydride to the hydriodic acid used, whilst Benedikt and Gruessner simplified the apparatus.

Certain modifications were recently proposed by the author[3] for simplifying and quickening the method without impairing its accuracy, and which at the same time presented special advantages for technical investigations. They

[1] *Oest. Ch. Ztg.*, 1898, Nos. 8 and 9.
[2] *Monatshefte für Chemie*, 1888, ix.
[3] *Ibid.*, 1895, xix.

consist mainly in replacing the tedious gravimetric estimation of silver iodide by the equally precise and quicker method of Volhard, the alcoholic normal silver solution being acidified with nitric acid in order to hasten the decomposition of the alkyl iodide.

In charging the Geissler apparatus the use of amorphous phosphorus suspended in water is replaced by a solution of equal parts of potassium carbonate and arsenious acid in 10 parts of water, thus avoiding the reduction of the silver nitrate, in the tube dipping into the first flask, by the amorphous phosphorus. The arsenious acid fixes any stray iodine, being itself oxidised to arsenic acid, whilst the excess of potassium carbonate fixes the hydriodic acid, liberating merely the innocuous gas $CO_2$.

Another advantage in the use of arsenious acid was discovered in the course of the work, viz. when a substance containing sulphur is subjected to the methoxyl test, and amorphous phosphorus suspended in water is used, the liberated sulphuretted hydrogen, which of course cannot be retained in the Geissler apparatus, precipitates silver sulphide from the silver nitrate solution.

This was already known to Zeisel,[1] who therefore abstained from applying the method to bodies containing sulphur.

In making methoxyl determinations with sulphurous resins the author observed a separation of arsenic sulphide in the Geissler apparatus charged with arsenious acid solution, but the silver nitrate in the receiver was free from traces of silver sulphide. It is necessary in such cases to keep the arsenious acid solution more dilute than usual, otherwise a copious deposition of arsenic sulphide may choke up the tubes of the Geissler apparatus.

[1] *Monatshefte für Chemie*, 1886, vii.

To simplify the calculation when Volhard's titrimetric method is used, a $\frac{n}{10}$ solution of silver nitrate is employed, dissolving 17 grms. of pure crystallised $AgNO_3$ in 30 c.c. of water, and making the solution up to 1 litre with commercial absolute alcohol. This solution is standardised against $\frac{n}{10}$ potassium thiocyanate, which in turn is titrated with aqueous $\frac{n}{10}$ silver nitrate. The strength of the alcoholic solution undergoes some change on keeping, and must therefore be tested from time to time.

For ordinary analyses it is sufficient to use 50 c.c. of the silver nitrate solution in the first flask, and 25 c.c. in the second, after acidification with a few drops of nitric acid free from nitrous acid. After the reaction is terminated—Zeisel's conditions being otherwise maintained throughout—the clear liquid above the silver iodide is poured off into a 250 c.c. measuring flask. The silver nitrate solution in the second flask is diluted with water and poured into the same measuring flask, the contents of which are thereupon made up to the mark with water, agitated well, and passed through a folded filter into a dry vessel.

For the titration, 50 or 100 c.c. of the filtrate are used, after suitable acidification with nitric acid (free from nitrous acid) and an addition of ferric sulphate solution.

The following example may serve as typical of the method:—

1·2064 grm. of Peruvian balsam was employed. Of the filtrate from the receiver—containing 75 c.c. $\frac{n}{10}$ silver nitrate solution made up to 250 c.c.—50 c.c. consumed 11·5 c.c. of $\frac{n}{10}$ potassium thiocyanate; consequently the total amount would consume $11{\cdot}5 \times 5 = 57{\cdot}5$ c.c. $\frac{n}{10}$ potassium thiocyanate, whilst the remaining 17·5 c.c. of $\frac{n}{10}$ silver nitrate was consumed in the production of silver iodide.

Now in order to determine the methoxyl value, it is

merely necessary to multiply by 0·0015 the number of c.c. of $\frac{n}{10}$ silver nitrate consumed, since 1 c.c. of $\frac{n}{10}$ silver solution is the equivalent of 0·0015 grm. of methoxyl. Hence in this case the methoxyl value is $0{\cdot}0015 \times 17{\cdot}5 = 0{\cdot}2625$, or, calculated to 1 grm. of Peruvian balsam, 0·0217, *i. e.* 21·7 per cent.

By using the Volhard titration the entire operation is complete within two hours, whereas with the Zeisel gravimetric method the work takes much longer. The values obtained by the two methods are very concordant, as evidenced in the examples published (*l.c.*), and the author, therefore, prefers the "titrimetric method."

The present is not a suitable occasion for discussing the value of these new methods, and all that need be said is contained in the following résumé of the author's paper (*Chem. Rev.*, 1899, No. 10):—

"In summing up, it may be stated that the newer methods of determining the acetyl value (K. Dieterich), carbonyl value (Kitt), methoxyl value (Gregor-Bamberger), may be welcomed as quantitative methods for characterising resins—provided they are properly applied to the appropriate resins—and also as supplementing the known methods of identification; but, owing to their limited applicability and tedious character, are by no means capable of replacing, far less superseding, the existing simple methods for determining the acid, ester, saponification, and other values which have proved so useful for identification and the detection of adulteration."

**Resin Acids; Resin Alcohols and their Characteristic Values.**—The author has repeatedly recommended the employment of the isolated resin acids and alcohols in connection with the analysis of resins. Naturally it would be necessary to accumulate further data, as these are at

present scanty, on such points as the difference between the resins and the pure resin acids—in ester-free resins—or the resin alcohols in resins containing esters. In this connection a comparison of the reactions, already given, of the resinotannols, and the cholesterin reactions of the constituents of resins will be found useful.

**Separation of Resin Acids and Fatty Acids.**—Gladding and Twitchell examined mixtures of fatty acids and resin acids, and the former recommended the following method for their separation :—

In the case of a fatty acid adulterated with resin, about 0·6 grm. of the substance is dissolved in 20 c.c. of 95 per cent. alcohol. To this solution is added a trace of phenolphthalein, and a solution of alcoholic potash is run in, drop by drop, from a burette, with continued stirring, until the indicator has assumed a dark red colour, characteristic of alkalinity.

After adding one or two drops of the potash solution in excess, the flask containing the liquid is placed on the water bath and the contents boiled for ten minutes. When cold, the whole is poured into a 100 c.c. test tube, the flask washed with ether, and—the whole being made up to 100 c.c. with this solvent—the tube is corked and shaken up thoroughly.

Next, 1 grm. of finely divided silver nitrate is introduced and shaken up well for ten to fifteen minutes, until the flocculent deposit of silver stearate or oleate has collected together at the bottom of the tube. Then 50–70 c.c. of the clear liquid are removed by means of a pipette, and transferred to another 100 c.c. test tube, where a further small quantity of silver nitrate is added to remove the fatty acid still in solution. The clear liquid is then mixed with 20 c.c. of dilute hydrochloric acid (one-third 21 per cent. HCl. and

two-thirds water); an aliquot part of the supernatant ethereal solution is evaporated in a platinum basin, the residue—dried in the steam oven and weighed—this being resin, accompanied by a little oleic acid. Direct experiment has shown that, under these conditions, 10 c.c. of ether retain on an average 0·00235 grm. of oleic acid, so that the results of the analysis may be corrected by means of this coefficient. The method is applicable to the determination of resin in linseed oil, soap, etc.

This method has been tried and modified by Ulzer and Defris,[1] who published the results they obtained in the quantitative estimation of fatty acids in presence of the resin acids of shellac and pine resin. They found a considerable difference in the behaviour of these two classes of resin acids. A dark sample of shellac furnished, by the Gladding method, only 13·76 per cent. of resin acids, the silver salts of which were for the most part insoluble in ether, whereas those from pine resin acids are soluble. When applied to the analysis of a mixture of 51 per cent. colophony and 49 per cent. shellac acids, the above separation method gave 48·46 per cent. of resin acids; but the concordance here experienced must be ascribed to a compensation of the sources of error, the colophony containing 12·9 per cent. of unsaponifiable constituents, and the shellac, 13·76 of acids resembling resin in character. A technical sample of varnish, composed of colophony and shellac, gave, after the expulsion of the alcohol, an iodine value 80·87, an acid value 111·30, and the saponification value 190·40, from which data the composition deduced was: colophony, 69·2 per cent., and shellac, 30·8 per cent. The separation method gave 63·7 per cent. of resin acids. From the above acid value, the composition would be expressed by: colophony,

[1] *Zeits. f. Analyt. Chem.*, 1897, p. 27.

59·3 per cent., and shellac, 40·7 per cent. Finally, the behaviour of the shellac acids in presence of the Twitchell method was examined, the result showing that, as in the case of fatty acids, the shellac resin acids form esters under the influence of a current of hydrochloric acid gas.

Copal resin acids were also examined by the Gladding and Twitchell method. It was found that the Gladding method could not furnish quantitative results, the reason for this being that a portion of the sodium soaps is separated from the alcoholic solution during neutralisation, the precipitation being increased by the subsequent addition of ether. The Twitchell method gave 81·01 per cent. of resin acids from Angola copal, and 86·37 per cent. from Cowrie copal.

Although belonging rather to the domain of fat analysis, the above method is referred to here because it is based on the different properties of fatty and resin acids, and because mixtures of resins and fats are largely used for technical purposes, and the chemist has frequently to undertake the separation of resin acids from fatty acids in resin analysis, just as the converse separation has to be effected in fat analysis. As Weger very rightly pointed out in his researches on oxygen absorption by resins, the above method cannot give more than relatively correct values, since, in the course of drying, the resin acids are subjected to the oxidising influences described by Weger, which affect the results to a considerable extent.

**Iodine and Bromine Values.**—We have already seen that, in a chemical sense, the relationship between fats and resins is, so to speak, *nil*, but that, nevertheless, the methods employed for the examination of the former substances can also be successfully applied to the latter. Less satisfactory, however, are the iodine values and the bromine values

determined by McIlliney, Mills, and Muter; but, according to K. Dieterich, these are of subordinate importance for the resins—as other authors have also shown, in special instances—the conclusions drawn from the iodine value being very liable to error, apart from the inaccuracy caused, in the determination of this value, by the dark colour of the liquid to be titrated and by the use of extracts instead of the natural drugs. The iodine value is, however, of great value in some cases, *i. e.* in the analysis of shellac and colophony.

**Suitable Quantitative Methods.** — The following quantitative methods are in use for, and are applicable to, the estimation of balsams, resins, and gum resins:—

(*a*) Acid value, by various methods.
(*b*) Ester value, direct or indirect.
(*c*) Saponification value, or resin value and gum value, by various methods.
(*d*) Percentage of moisture.
(*e*) Ash.
(*f*) Percentage soluble in alcohol.
(*g*) Percentage insoluble in alcohol.
(*h*) Specific gravity.
(*i*) Percentage soluble in other solvents.

Further:

(*k*) Iodine value.
(*l*) Special determinations, such as cinnamein and resin esters in Peruvian balsam.
(*m*) Identity reactions, partly coinciding with *a*, *b*, and *c*.
(*n*) Acetyl, carbonyl, and methoxyl values.
(*o*) Examination of the resin acids and resin alcohols.
(*p*) Qualitative reactions.

According to the nature of the substance under examination the following methods of determining the important acid and saponification values are available.

**Systematic Résumé of the Performance of the Acid and Saponification Value Tests.**

*A.* Acid Value.

1. By direct titration:

($\alpha$) Of the complete solution of the soluble resinous matter in alcohol, chloroform, etc.

*Performance.*—1 grm. of the substance is dissolved in a suitable solvent or mixture, and is titrated with alcoholic $\frac{n}{2}$ or $\frac{n}{10}$ caustic potash in presence of phenolphthalein, until a red coloration is produced.

*Examples.*—Nearly all such resins as are soluble, and for which no special method has yet been prepared.

($\beta$) After the preparation of an alcoholic extract, in the case of imperfectly soluble resins, the said extract being employed for titration.

*Performance.*—Exactly similar to $\alpha$, except that the result is calculated to 1 grm. of the extract instead of 1 grm. of the crude product.

*Examples.*—Gum resins, benzoin, storax.

($\gamma$) Of the solution obtained by extracting a partially soluble resin with alcohol and water.

*Performance.*—One grm. of the finely ground resin is extracted by boiling with 30 c.c. of water under a reflux condenser for fifteen minutes, followed by an addition of 50 c.c. of 96 per cent. alcohol, and re-boiling for an equal period. After cooling, the extract is titrated, without

filtration, with $\frac{n}{2}$ alcoholic caustic potash and phenolphthalein, until a red coloration appears.

*Examples.*—Myrrh, bdellium, opopanax, and sagapenum.

2. By back titration :

($\alpha$) In the case of entirely (or nearly) soluble resins, free from esters, where the alkali combines with the acid, and at the same time dissolves the whole of the resin.

*Method.*—One grm. of the finely divided (ester-free) resin is left in contact with 25 c.c. of $\frac{n}{2}$ alcoholic potash and 50 c.c. of benzine in a stoppered flask for twenty-four hours—or until solution has been carried as far as possible—and is then titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein.

*Examples.* — Dammar, sandarach, mastic, guaiacum, copal, etc.

($\beta$) In the case of partially soluble—esteriferous, but sparingly saponifiable—resins, where the alkali fixes the acid and extracts the acid constituents.

*Method.*—One grm. of the finely powdered substance is left for twenty-four hours in contact with 10 c.c. of alcoholic $\frac{n}{2}$ potash and 10 c.c. of aqueous $\frac{n}{2}$ potash in a stoppered flask; it is then mixed with 500 c.c. of water and titrated back.

*Examples.*—Asafœtida, olibanum.

($\gamma$) Resins that are only partially soluble and contain esters, an aqueous alcoholic extract being employed.

*Method.*—One grm. of the finely divided resin is boiled for fifteen minutes under a reflux con-

denser with 50 c.c. of water, after which 100 c.c. of strong alcohol are added and the whole is boiled up again for another fifteen minutes. After cooling, the liquid and substance are made up to 150 grms. and filtered, 75 c.c. of the filtrate (= 0·5 grm. of substance) being treated for exactly five minutes with 100 c.c. of alcoholic $\frac{n}{2}$ potash, and then titrated back with $\frac{n}{2}$ sulphuric acid.

*Examples.*—Ammoniacum, galbanum, gamboge.

($\delta$) In the case of resins which contain esters, are almost entirely soluble, and saponify readily: the natural drugs are used.

*Method.*—Ten c.c. of $\frac{n}{2}$ alcoholic potash are left to act for five minutes on the finely divided natural drug, and the solution is then titrated back.

*Example.*—Benzoin.

3. *By estimating the volatile acids* (in the case of gum resins rich in ethereal oils.

*Method.*—One-half grm. of the substance is suffused with a little water in a flask, and a current of steam is passed through, the flask being placed on a sand bath to prevent excessive condensation. The receiver is charged with 40 c.c. of aqueous $\frac{n}{2}$ potash, into which dips the tube from the condenser. Exactly 500 c.c. of distillate are collected, the condenser tube is swilled out well with distilled water, and the whole is titrated back in presence of phenolphthalein. In this case the acid value gives the number of mgrms. of KHO neutralised

by 500 c.c. of distillate from 0·5 grm. of resin.

*Examples.*—Ammoniacum, galbanum.

*B.* Ester Value.—This is always ascertained indirectly by calculation, *i. e.* subtracting the acid value from the saponification value, except in cases where the acid value has been determined as under *A.* 3, and where a resin value and total saponification value are present. In such event the ester value cannot be calculated.

*C.* Saponification Value.

1. By the hot method:

($\alpha$) In the solutions of completely soluble resins.

*Method.*—One grm. of the resin is dissolved and kept on the boil for half an hour in a steam bath, with 25 c.c. of alcoholic $\frac{n}{2}$ potash, under a reflux condenser. After dilution with alcohol, the whole is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein.

*Examples.*—Nearly all balsams and resins for which no special methods have been devised.

($\beta$) With a previously prepared alcoholic extract of a partially or sparingly soluble resin.

*Method.*—The same procedure exactly as under $\alpha$, except that an alcoholic solution of the extract is taken, the results being calculated to 1 grm. of the crude drug, and not of the extract.

*Examples.*—Gum resins, benzoin, storax.

($\gamma$) As $\alpha$, except that the crude drug is taken after an addition of water to dissolve out the gummy matter.

*Example.*—Myrrh.

2. Cold method:

($\alpha$) For perfectly soluble resins, with cold alcoholic alkali and benzine only.

*Method.*—One grm. of the substance is treated in a stoppered 500 c.c. glass flask with 50 c.c. of benzine (sp. gr. 0·700 at 15° C.) and 50 c.c. of alcoholic $\frac{n}{2}$ potash. After standing for twenty-four hours at room temperature, it is titrated back with $\frac{n}{2}$ sulphuric acid; in the case of Peruvian balsam, for instance, about 300 c.c. of water must be added to dissolve the precipitated salts.

*Examples.*—Peruvian balsam, copaiba balsam, benzoin, storax.

($\beta$) Fractional saponification, including "resin value" and "gum value," in the case of imperfectly soluble resins—alcoholic and aqueous alkali, with an addition of benzine to each, being used in succession.

*Method.*—Two samples, each of 1 grm., of the resin are powdered and suffused in separate 1 litre stoppered flasks with 50 c.c. of benzine (sp. gr. 0·700 at 15° C.), followed by 25 c.c. of alcoholic $\frac{n}{2}$ potash. After standing (closed) for twenty-four hours at room temperature, with frequent shaking, the one sample is shaken up with 500 c.c. of water and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein; this gives the resin value. The second sample is then treated further with 25 c.c. of aqueous $\frac{n}{2}$ potash and 75 c.c. of water, and is left for another twenty-four hours, with frequent shaking, being finally diluted with 500 c.c. of water and titrated

back as above. This gives the "total saponification value," the difference between this and the resin value being the "gum value."

*Examples.*—Ammoniacum, galbanum, gamboge.

### Iodine Value

**Hübl's Process.**—For the estimation of the iodine number or value by this process, the following solutions are required :—

A. A solution containing 25 grms. of iodine in 500 c.c. of absolute alcohol.

B. A solution containing 30 grms. of mercuric chloride in 500 c.c. of absolute alcohol.

These are mixed in equal volumes and allowed to stand 24 hours before being used.

C. Decinormal sodium thiosulphate solution containing 24·8 grms. of the salt in 1 litre. This is accurately standardised against pure iodine at frequent intervals. The addition of about half a grm. of ammonium carbonate to this solution helps to preserve its strength, which otherwise deteriorates rapidly.

D. Potassium iodide solution 10 per cent. strength.

E. Starch solution made by dissolving about 5 grms. of soluble starch in 100 c.c. of boiling water and allowing to cool.

F. Pure chloroform.

The estimation of the iodine value is performed as follows : 0·25 to 1·0 grm. of the finely-powdered substance is weighed into a dry stoppered flask, 10 c.c. of chloroform is added and the mixture heated, it is then cooled and 30 c.c. of the Hübl solution is added. The flask is stoppered and

kept in a cool dark place, being shaken from time to time. Owing to the slowness of the action in many cases the time should be prolonged, say, to 18 hours. If the liquid loses colour rapidly more Hübl's solution should be added, as it is essential that this should be kept in large excess, the total iodine added being at least double the amount absorbed.

At the conclusion of the time allowed 10 c.c. of the potassium iodide solution is added and the mixture well shaken, after which 20 c.c. of water is run in and the liquid titrated with the thiosulphate solution, using the starch solution as indicator when the yellow colour of the solution has become faint.

A blank test is at the same time carried out, using 10 c.c. of chloroform and the same amount of Hübl's solution, allowing it to stand the same length of time as the sample. The iodine used by the resin is found from the difference in the two titrations and is calculated on 100 parts of the resin.

The Hübl test suffers from the defect that the whole of the resin is rarely soluble in chloroform; in fact, in many cases the reverse is the case, a considerable proportion remaining undissolved, and this either is not acted upon or is only affected to a limited extent by the Hübl solution. In some cases, *e. g.* shellac, absolute alcohol is used in place of chloroform for dissolving the material.

**Wijs Process.**—The Wijs process is a development of the Hübl process, differing from it principally in the fact that iodine monochloride is used in place of the iodine, the solution becoming thereby very much more active. Thus with the Wijs solution the time of action may be shortened to one-half to one hour, and rarely requires more than six hours. With substances such as oils and fats which are

readily acted upon, and provided that sufficient time is allowed in the case of the Hübl solution, the results are practically the same with both solutions; but when the material is not readily acted upon, and this applies to most resins, then the Wijs solution, being more active, yields much higher figures. Provided, however, that the process used is known and the time of action is recorded, no difficulty occurs in interpreting the figures.

It is very desirable, however, especially in resin analysis, that a definite method and procedure should be agreed upon in order to simplify the matter, and at the same time place the figures upon a comparable basis.

Wijs solution is made as follows :—

A. By dissolving 7·9 grms. of iodine trichloride in 500 c.c. of glacial acetic acid by gentle heat.

B. By dissolving 8·7 grms. of iodine in 500 c.c. of glacial acetic acid.

The two liquids are then cooled and mixed to make 1 litre of the solution.

C. Pure carbon tetrachloride.

The other solutions are the same as those for the Hübl process, and the method is exactly the same, only that 10 c.c. of carbon tetrachloride is used as the solvent in place of chloroform. Many resins are, however, soluble in glacial acetic acid, so that this may be used as the solvent.

Another method of preparing the Wijs solution is to dissolve 13 grms. of iodine in glacial acetic acid and pass into it dry chlorine gas until the colour just commences to change, it is then made up to 1 litre with the glacial acetic acid.

By reason of the analytical labours of Kremel—who was

the first to systematically transfer to resins the quantitative methods employed for fats, though he was closely followed by von Schmidt, Erban, Mills, Williams, Beckurts and Brüche, E. Dieterich, etc.—and others, a large collection of experimental material has been accumulated. From these a number of general and particular axioms have been deduced by K. Dieterich, who has also employed as a basis the results of his own investigations into Peruvian balsam, Copaiba (Angostura, Bahia, Carthagena, Illurin, Para, Maracaibo, Surinam, Gurjun) balsam, Mecca balsam, Benzoin (Siam, Sumatra, Padang, Palembang, Penang), Colophony, Copal, Dammar, Elemi, Palm dragon's-blood, Socotra dragon's-blood, Guaiacum, Mastic, Sandarach, Storax, Thapsia resin, Anime, Caranna resin, Labdanum, Turpethum resin, Ammoniacum, Asafœtida, Galbanum, Myrrh, Bdellium, Opopanax, Sagapenum, and Olibanum. These axioms are now given with the corresponding examples for those of a special character :—

**General Axioms.**—Generally speaking, the great fluctuations hitherto noticed in the analytical values obtained with resins—apart from the divergences *à priori* due to the variable composition of the resins themselves—are attributable to the following factors :—

1. The lack of uniform, rational methods, with well-defined conditions of performance.
2. The scant individualisation of the current methods, and disregard of the modern chemistry of the resins.
3. The use of extracts in place of the natural drugs.
4. The lack of tests performed on authentically pure resins, taken direct from the parent trees, as a basis for the determination of values. (Up to the present

time only a few authentically pure resinous bodies, such as Peruvian balsam, storax, and a few others, have been examined.)

According to K. Dieterich the following points should be considered in attempts to improve resin analysis :—

1. The use of the natural drugs instead of extracts.
2. The prescription of uniform conditions in the performance of rational methods.
3. Individualising these methods on the basis of modern resin chemistry.
4. Employment of quantitative methods in preference to qualitative methods—especially colour reactions.
5. Fixing normal limits for constant values, on the basis of the examination of authentically pure samples taken direct from the parent trees.

The following " special " points should be borne in mind in resin analysis :—

**Special Axioms with Examples.**—I. In any circumstance it is erroneous to employ only a portion—*e. g.* an alcoholic extract—of a resin or gum resin for analysis. When this is done, there occur—as already shown in the case of Siam and Sumatra benzoin, storax, myrrh, ammoniacum, galbanum, etc.—losses and alterations which influence the results and preclude the formation of an accurate opinion on the natural drugs themselves. On this account the greater proportion of the resin values recorded in the literature of the subject, having been obtained in this imperfect manner, are restricted to a merely relative utility. The values obtained by using an extract cannot therefore in any case be regarded as applicable to the crude product.

II. Still less acceptable are values obtained by using 1 grm. of extract instead of the amount of extract corresponding to 1 grm. of crude drug, since 1 grm. of extract is equal to much more than 1 grm. of crude drug; moreover, it represents a variable quantity of the original drug in different cases, and therefore furnishes values in no way approximating to the definition "acid value" or "ester value."

III. Where possible, the previous preparation of a hot alcoholic solution without employing a reflux condenser, etc., should be avoided, as liable to cause a loss of volatile matters, especially in the case of substances that are sparingly or only partially soluble (*e. g.* gum resins, storax, etc.).

IV. All methods employing back titration are practical, because they utilise the alkali both for fixing the acid and, at the same time, for acting as a solvent; they also yield a better end reaction (red into yellow) than the ordinary direct titration methods (for ammoniacum, galbanum, asafœtida, benzoin, olibanum, etc.).

V. With some resins (mostly free from esters) it has been found that, although soluble in inert solvents, the acid is not quantitatively and promptly fixed in direct titration methods; consequently they must be treated by the back titration method, and time must be given for the fixing of the resin acids. (To these resins belong: guaiacum, copal, dammar, sandarach, mastic, etc.). In this case also the end reaction is very well defined (colour-changed red to yellow).

VI. Again, in the case of ester-free or sparingly saponifiable resins which can be titrated direct with but slight variation, the back titration method is preferable for determining the acid value, because no preliminary solution is required, the alkali itself serving as a solvent, and giving a

sharper end reaction from red to yellow than is possible with the converse change. The values obtained are generally more concordant than those obtained in the direct method.

VII. Earlier saponification tests were frequently unreliable, the values furnished were merely imperfect, or the dark-coloured liquids produced were difficult to titrate, contained decomposition products, or furnished merely relatively useful values because of the use of extracts in place of the natural drugs (*e. g.* Peruvian balsam, Siam benzoin, Sumatra benzoin, etc.).

VIII. Provided the natural drugs be used, the best results are furnished by the cold and fractional saponification methods, mainly because the liquids obtained are lighter in colour and more readily titrated.

It has been found that many resins can be saponified in the cold by alcoholic alkali and benzine, and many by the conjoined action of aqueous and alcoholic alkali in the cold. The first type of method is known as "cold saponification," the other as "fractional saponification"; in the latter the value given by the alcoholic alkali and benzine is termed the "resin value," and the result furnished by the aqueous and alcoholic alkali is the "total saponification value."

Furthermore, it has been found that nearly all the balsams, and many resins, can be completely saponified in twenty-four to forty-eight hours, without heat, by the simple cold method; and several of the gum resins and other bodies containing gum in addition to resin (except myrrh, olibanum, and asafœtida) can be effectually dealt with by the fractional method in the same time. However, with some gum resins it appears that only the fixation of the acid is affected by this means, without any saponification being produced.

The following are saponified in twenty-four to forty-eight hours by the cold process :—

Peruvian balsam.
Copaiba balsam (Angostura, Bahia, Carthagena, Maracaibo, Maturin (East Indian), Para (West Indian) balsams)
Benzoin (Siam, Sumatra, Palembang, Padang, Penang)
Myrrh
Storax
Mecca balsam

} By alcoholic alkali and benzine.

Ammoniacum
Galbanum
Euphorbium
Gamboge
Dragon's-blood (Socotra, Sumatra)
Lactucarium

} By fractional saponification.

On the other hand, the following cannot be saponified by either method within the time specified :—

Asafœtida
Olibanum

} The use of alcoholic and aqueous alkali merely fixes the acids.

It should be noted that the benzine should on no account be omitted, although for the most part it dissolves imperfectly.

IX. For the prevention of error, the acid and saponification values should be determined in two separate experiments.

X. In order to obtain solutions as free from colour as possible, only 1 grm. of any balsam, resin, or gum resin should be taken, instead of 3 grms. as in the case of fats. The increased margin of error in titration is not so great as the errors arising in the titration of darker liquids. Moreover, experiment has shown that the values obtained from 1 grm. are perfectly concordant with those furnished by

3 grms., but the end point in the former case is usually more easy to detect.

XI. Dilution, whether of a solution or a saponification liquid, should rarely if ever be practised with water, alcohol being generally the best for this purpose: the methods prescribed in each case should be carefully followed. Water usually produces a milky turbidity, and forms a liquid difficult to titrate; or decomposition of the resin soap may ensue, as in the case of colophony, dammar, copal, etc., with liberation of free alcohol. For this reason the use of, as far as possible, " water-free " diluents is advisable.

XII. The end reaction being quicker and better defined when $\frac{n}{2}$ alkali is used than with $\frac{n}{10}$ alkali, and the puzzling intermediate colour-changes not occurring, it is always better to use the stronger alkali, despite the inherent errors in titration attending thereon.

XIII. Since the natural drugs, and not portions thereof, should always be used, it is very necessary to secure a good average sample, which is best obtained by grinding at least 100 grms. of the dry drug as finely as possible (see XXIII.). Balsams should always be well shaken or stirred beforehand; resins containing water, *e. g.* storax, should be freed from moisture and stirred up well together. Gum resins, which are very soft and difficult to pulverise, are cooled by immersion in a refrigerant if necessary, and pulverised repeatedly until a good average sample is prepared, warmth being avoided in any event. When the parcel is large—entire boxes of benzoin, casks of storax, or bales of gum resin—the samples should be drawn from various parts of the bulk and not merely from one place. If, as is the case with myrrh, ammoniacum, galbanum, opopanax, and sagapenum, the gum resins are used direct, it is essential that the substance should be dissociated by boiling successively with

alcohol and water, under a reflux condenser, especially before determining the acid value (whatever the method employed).

XIV. Naturally a single analysis is never sufficient to afford grounds for an opinion in the examination of resins, duplicate determinations being essential, and the mean of the results must be taken. For cold saponifications, especially when the liquids must be left to stand a long time, stoppered glass flasks should alone be used. Resins or balsams, which owing to their sticky or semi-fluid nature are difficult to handle, should be weighed on a glass rod, which is then placed, along with the substance, in the saponification liquid or glass flask.

XV. All results should be calculated to the natural crude drug, and not, as is frequently done, to the goods dried at 100° C. Or, better still, both values should be given together.

XVI. The determination of the iodine and bromine values is, except in a few instances, of little importance, being in the first place a frequent source of error, and also furnishing inaccurate values by reason of the difficulty in detecting the end-point. (The iodine values of nearly all the resins and balsams have been determined—in the former case from the alcoholic extracts.)

XVII. Resins containing acids and esters can furnish acid and saponification values, whereas such as contain merely esters or free resin acids, can only yield the corresponding saponification or acid value, as the case may be.

Thus it is impossible to speak of the "acid value" of dragon's-blood, this body containing no free acids; or of the "ester values" of ester-free resins like colophony, sandarach, copal, dammar, etc. Values of this kind recorded in the literature of the subject are useless, and should be eliminated.

XVIII. Quantitative methods are all preferable to those of a qualitative character, the best of all being such as

relate not merely to subordinate constituents of the resins, present in small amount therein, but such as are concerned with the principal components. In addition, no methods can claim to have any real worth except they have been found reliable when systematically applied to adulterated resins as well as to the pure substances.

XIX. As with fats, the acetyl value furnishes some guidance in forming an opinion, the more so, because nearly all the resins contain oxyacids.

Thus, the acetyl products of the turpentines vary considerably from one another and from the initial product. Similar conditions prevail in the case of dammar, copal, etc. (see *Helfenberger Annalen*, 1897, pp. 39–44). Of the carbonyl and methoxyl values, as well as the resin alcohols and acids, mention has already been made.

XX. Generally speaking, the methods used in the examination of fats and oils are also applicable to the balsams, resins, and gum resins, though it should be borne in mind that the resins—being mixtures that have probably sustained considerable alteration in collection and by external influences, and not always homogeneous substances —cannot be investigated by any single method applied to the whole, but that it is necessary to fit the methods to the special resin, balsam, or gum resin under examination. Even a slight deviation from the lines already laid down with precision will bring about changes in the results.

XXI. Phenolphthalein has proved the best indicator for the, oftentimes strongly coloured, titration liquids. Other indicators, such as tropæolin, hæmatoxylin, litmus, rosolic acid, methyl orange, and alkali blue, have all had to be discarded as useless.

XXII. The alcoholic potash solution used for the cold and fractional saponification tests should be as rich as possible

in alcohol, *i. e.* 96 per cent. spirit is used, and the liquid is filtered off from the insoluble $K_2CO_3$.

XXIII. In comminuting and reducing to powder the resins (see VIII.), gum resins, and all products that are sticky when rubbed together, prolonged heating in a drying oven, or even a preliminary warming, must be avoided on account of the aromatic constituents, and the end in view must be attained by storing the substances in a very cool place so as to render them hard and easily pulverable. Where this work has to be done on a large scale it is advisable to carry on the operation in the winter time.

**Transition Stages of Resinous Bodies and their Nomenclature.**—A few words as to the nomenclature of the resins, the transition of one form of resin into another, and their mutual relation. Since we use names—such as dammar, copal, elemi, copaiba, etc.—which are more genetic than specific, it follows, as a matter of course, that confusion is liable to occur. Special mention will be made in Part II. of this indefinite nomenclature, with particular reference to the transition stages between kino and dragon's-blood, bdellium and myrrh, turpentine resins and dammar or copal; the, to some extent, nearly allied names, such as: resina caranna, gomart gum, resina kikekunemalo, anime, tacamahac, elemi, etc. The variations in the names of commercial grades also frequently lead to much confusion.

# PART II

## INTRODUCTION

Before proceeding to specially consider the various resinous substances separately, a few general remarks are necessary.

In dealing with the estimation of the acid, ester, and saponification values, the expression "usual method" implies the method performed in the same manner as in the case of fats—*i. e.* the Hübl method—without any special modification. Thus the acid-value determination consists of: solution in alcohol, and direct titration with $\frac{n}{2}$ alkali and phenolphthalein; the saponification-value method is: boiling for half an hour under a reflux condenser, and titrating back after cooling, the reagents used being alcoholic $\frac{n}{2}$ alkali, and aqueous $\frac{n}{2}$ sulphuric acid. The ester value is found by difference, as already described in Part I.

The estimation of "matters soluble in petroleum ether" by the Hirschsohn method, so frequently referred to, is effected by extracting the substance with petroleum spirit, of boiling point 40°, 60°, or 80° C., and drying the extract at 120° C. until of constant weight. In other cases the solution is evaporated at 17° C., and the residue weighed till constant. Where the above temperatures are referred to in this connection, they must be taken to express the same meanings as here involved; and all specific gravities refer to 15° C., unless another temperature is specially mentioned.

The following practical hint may be given in connection

with the analysis of resins and the necessary weighings appertaining thereto :—In the case of such resins as soft elemi, storax, etc., which are of a greasy or balsamic character, weighing out into narrow-necked litre flasks (for cold and fractional saponification) is inconvenient by reason of the resin adhering to the rim and taking a long time to run down. It is then better to place a small quantity of the resin on a tared watch glass, and weigh the whole, take up about 1 grm. by means of a small glass rod, and insert rod and all into the flask; the loss in weight of the watch glass and contents then shows the quantity of resin taken for analysis. Thus the above-mentioned inconvenience is avoided. The preparation of average samples has already been discussed under axiom XXIII. (Part I.).

**Definitions.**

1. The *acid value* (direct and indirect) = the number of mgrms. KHO neutralised by the free acid in 1 grm. of resin during direct or back titration.

2. The *acid value of the volatile portion* = the number of mgrms. KHO neutralised by 500 grms. of distillate obtained from 0·5 grm. of gum resin (ammoniacum, galbanum) by distillation with steam.

3. The *saponification value* (hot and cold) = the number of mgrms. KHO neutralised by 1 grm. of resin in hot or cold saponification.

4. The *resin value* = the number of mgrms. KHO neutralised by 1 grm. of certain resins and gum resins on cold fractional saponification with alcoholic alkali by itself.

5. The *total saponification value* (fractional saponification) = the total number of mgrms. KHO neutralised by 1 grm. of certain resins and gum resins on cold fractional saponification with alcoholic and aqueous alkali in succession.

6. The *gum value* = the difference between the total saponification value and the resin value.

7. The *ester value* = the difference between the saponification value and the acid value.

8. The *iodine value* = the amount of iodine absorbed by 100 parts of the resin. The method of determining this should be indicated.

9. The *acetyl value* = the difference between the acetyl saponification value and the acetyl acid value.

10. The *carbonyl value* = the percentage of carbonyl oxygen in the substance taken.

11. The *methoxyl value* = the amount of methoxyl furnished by 1 grm. of resin.

In the first edition of this book abbreviations were given for the different methods of determining these constants, but these have been eliminated as they were found to serve no useful purpose. In all cases the methods employed are indicated.

The calculations are based on the new table of atomic weights drawn up by Landolt, Ostwald, and Seubert, and adopted by the German Chemical Society.

## CHAPTER I

BALSAMS

### 1. Canada Balsam.

*Balsamum Canadense.*

**Origin and Habitat.**—*Abies balsamea*, DC. (Coniferæ). North America.

**Chemical Constituents.**—Levo-rotatory ethereal oil, 18·6 per cent.; resin soluble in alcohol, 46 per cent.; resin sparingly soluble in alcohol, 33·4 per cent.; caoutchouc, 4 per cent.; bitter principles, extractives, traces of acetic acid, 4 per cent. (Bonastre). See also p. 334 *et seq.*

By fractional separation from methyl alcohol (see *Schweiz. Wochenschr. f. Chem. u. Pharm.*, 1899, No. 44; and *Ph. Ztg.*, 1899, No. 77) Tschirch has recently succeeded in isolating, from the resin from *Abies Canadensis*, "crystalline" resinol acids, which stand in a certain relationship to abietic acid (Mauch) and pimaric acid (Vesterberg).

**General Properties and Commercial Varieties.**—Canada balsam is of the consistency of honey but more viscous, perfectly clear, pale yellow (almost greenish) in colour, and slightly fluorescent. The odour is agreeably aromatic, the flavour bitter, and it yields a bitter principle when treated with hot water. The balsam is only partially soluble in absolute alcohol. (See also under Turpentines, Tereb. argentoratensis, Strasburg T.)

**Adulterants.**—Colophony, Venice turpentine.

**Analysis.**—In general the available analytical data are

meagre. Hirschsohn found that Canada balsam is soluble in petroleum ether, except for a small residue, but that the subsequent addition of more solvent produced turbidity.

A. Kremel found—

Acid value (direct) = 83·0
81·3

by dissolving about 1 grm. in strong alcohol and titrating direct with alcoholic $\frac{n}{2}$ potash. The ester value and saponification value were not estimated.

F. Dietze found—

| | I. | II. | III. |
|---|---|---|---|
| Acid value (direct) . . . | 84·89 | 85·93 | 84·40 |
| Ester value . . . . | 4·54 | 9·83 | 9·00 |
| Saponification value (hot) . | 89·43 | 95·76 | 93·40 |

the acid value being determined by the method practised by Kremel, and the saponification value by the "usual method" (see Introduction to Part II.).

E. Dieterich's results are as follows:—

Acid value (direct) = 84·0–86·8.

Solubility in—

Chloroform, Acetic ether, Benzol } complete.
Ether, Oil of turpentine } almost to quite complete.
90 per cent. alcohol, up to 90·90–93·58 per cent. turbid solution.
Petroleum ether, 83·46–92·73 per cent.

The methoxyl value was found to be nil by Gregor and Bamberger.

(For the detection of colophony in resins and balsams by the Storch-Morawski method, see under Colophony.)

Evans has compared Oregon balsam with Canada balsam, the figures being as follows :—

| | Oregon Balsam. | Canada Balsam. |
|---|---|---|
| Acid value (direct) | 80 | 79·6–98 |
| Saponification value (hot) | 86 | 87·5–105 |
| Acid value of resin | 152·6–153 | 107·8–123 |
| Specific gravity of essential oil | 0·865–0·867 | 0·860–0·862 |
| Optical rotation of oil in 100 mm. tube | − 36°–37° 24′ | − 26′–28° 56′ |
| Refractive index at 20° | — | 1·5194–1·5213 |

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## Copaiba Balsam.

*Balsamum Copaivæ* (*D. A. III.*).

**Origin.**—Various Copaïferæ, such as *Copaïfera officinalis* and *guianensis*, *C. multijuga*, etc. (Cæsalpinaceæ).

**Habitat.**—South America, East Indies, Africa.

**Chemical Constituents.**—Ethereal oil, 40–60 per cent.; (sp. gr. ·895–·918; B.P. 250°–275°; optical rotation in 100 mm. tube − 6° to − 40°; contains caryophyllene according to Wallach). Resin, 60–40 per cent.

The ethereal oil corresponds to the formula $C_5H_8$ = $C_{15}H_{24}$ (Berthelot), or $C_{20}H_{32}$ for Para balsam (Engländer), $C_5H_{24}$ (Densen and Hehn). The resin is soluble in alcohol, benzol, and amyl alcohol, and consists chiefly of amorphous acids—copaibic acid ($C_{20}H_{30}O_2$), however, being crystalline (Schweitzer); Para balsam contains oxycopaibic acid, $C_{20}H_{28}O_3$ (Fehling); Maracaibo balsam contains metacopaibic acid, $C_{22}H_{34}O_4$ (Strauss); and bitter principles have been detected in all the varieties of this balsam. Tschirch

and Keto found in Para balsam paracopaibic acid ($C_{20}H_{32}O_3$, M.P. 142–145°), and homocopaibic acid ($C_{18}H_{28}O_3$), in Maracaibo balsam a crystalline resin acid ($C_{11}H_{16}O_2$, M.P. 89°–90°), and in Illurin balsam, Illurinic acid ($C_{14}H_{20}O_2$, or $C_{21}H_{30}O_3$, or $C_{20}H_{23}O_3$, M.P. 128°).

**General Properties and Commercial Varieties.**—Of the two principal classes of copaiba balsam, the thick and the thin, Maracaibo (Venezuela) balsam may be taken as representing the former type, and Para (Maranham) balsam the more fluid class, the other varieties being mostly intermediate. The majority, like Gurjun balsam, exhibit strong green fluorescence. The chief commercial varieties are Maracaibo and Para. Latterly Maturin balsam has been recommended as a substitute for the thick officinal Maracaibo balsam, as was formerly the case with Angostura and Carthagena balsams. All the varieties have a very strong and aromatic odour, and a bitter, irritant taste (sp. gr. ·916–·969). Bahia, Carthagena, Surinam, Angostura, and "West African" (Illurin, Antilles) balsams are now seldom found in commerce. According to Hartwich, a balsam ("baume à cochon") similar in action to copaiba is obtained from *Hedwigia balsamifera* (Burseraceæ family), and *Humiria floribunda* yields a balsam which smells like benzoin and is used as a remedy for gonorrhœa (Hartwich).

**Adulterants, etc.**—The officinal balsams are adulterated with Gurjun balsam, fatty oils (ricinus oil, olive oil), storax, colophony, turpentine, sassafras oil,[1] oil of turpentine, paraffin oil, etc., whilst the other balsams are frequently mistaken for, or adulterated by, one another. Maracaibo balsam is mostly falsified with thin Para balsam.

**Analysis.**—With the exception of Peruvian balsam there

[1] This oil is, however, dearer than copaiba balsam, and is therefore unlikely to figure in practice as an adulterant of the latter.

is probably no balsam that has been so widely examined as copaiba, nearly all the known varieties, such as Angostura, Bahia, Carthagena, Maracaibo, Maturin, Gurjun, Para, Surinam, and West African balsams, having been tested. That Maracaibo balsam, being the officinal medicament (D.A. III.), has been examined with particular frequency, goes almost without saying. The main reason for the great variations in the results obtained by different workers is the almost entire absence of a really pure balsam among the commercial grades, adulteration being both frequent and varied. Mention of this circumstance has been made by Gehe & Co., *The Oil Paint and Drug Reporter*, and (more recently) by K. Dieterich. An innumerable array of qualitative reactions and modifications of the same has been recorded by Ulex, Wagner, Maisch, Proeter, Guibourt, Dierbach, Raleigh, Chrestien, König, Lowe, Gerber, Rose, Thorn, Gutnik, Vigne, Vallet, Redwood, Hager, Wimmel, Gehe & Co., Enell, Muter, Hirschsohn, Maupy, and others. The first large and comprehensive work on the various copaiba balsams was published by E. Praël, who also determined the content of resins and ethereal oils; and subsequently, quantitative methods for determining the acid, ester, and saponification values, and the sp. gr., were introduced by A. Kremel. The utility of these values is the subject of much difference of opinion, for whereas Beckurts and Brüche declare in favour of the iodine value, others—Wimmel, Gehe & Co., and more recently, K. Dieterich—think little of this test. Nearly all authors, however, are unanimous in recommending the quantitative determination of the acid, ester, and saponification values, and the fixing of a standard of specific gravity; but so long as pure and uniform products are unobtainable in commerce no reliance can be placed on the Hager optical rotation method (Maracaibo balsam dextro-,

nearly all commercial balsams levo-rotatory); the acid test as given in the German Pharmacopœia (D. A. III.), or by Enell; the ammonia test of Gehe & Co., Wimmel, and Bosetti; or the Grote agitation test. The only possible way of valuing the balsams is by making quantitative determinations of the above-named constants, and by fixing limits of fluctuation within which variation is permissible for the various balsams. This plan has been latterly recommended by Cæsar & Loretz, and by Gehe & Co., as a progressive step, though, of course, as pointed out by Thoms, methods so imperfect as those given in the German Pharmacopœia are inapplicable. With regard to fixing a margin of permissive variation, this will have to be postponed, Gehe & Co. having found that some adulterated balsams give values within the limits set up by K. Dieterich for the pure products; and it will not be until we can obtain samples of undeniable purity that reliable limits can be laid down for copaiba balsams. On the other hand, the author differs from Gehe & Co., in that he attributes a merely subordinate importance to the qualitative tests with ammonia and colophony (Bosetti's method). Owing to the variable proportion of ethereal oil and copaiba resin, the method prescribed for determining these constituents by the British Pharmacopœia has as little to recommend it as the iodine value test. However, it seems advisable to determine in the various individual balsams the percentage of matters extractable by various solvents, as was formerly done with nearly all known resins by E. Dieterich, in continuance of the values obtained by Hirschsohn, von Schmidt and Erban, Muter, Praël, and others. The qualitative colour reactions are not included in the present work, as they are not reliable. The Mauch method for observing the colour reactions furnished by the ethereal oil extracted by chloral hydrate is perhaps an

improvement, so far as the accuracy of the colour reactions themselves; although these, like others of the same class, are always more or less unreliable. Nevertheless, the value of his method in showing that ethereal oils can be easily isolated by chloral hydrate should not be under-estimated.

Gregor and Bamberger's methoxyl values cannot usefully be quoted, the authors having omitted to state which balsams were examined.

## 2. Angostura Copaiba Balsam.

The information available about this balsam is rather scanty.

Praël found—sp. gr. 0·980–1·009; resin, 59·90 per cent.; ethereal oil (sp. gr. 0·906), 40·10 per cent.

Beckurts and Brüche found—

| | |
|---|---|
| Acid value (direct) . . . | 99·6 |
| Ester value . . . . | *nil* |
| Saponification value (hot) . | 99·6 |
| Sp. gr. . . . . | 1·022 |

Gehe & Co. seek to have the Angostura balsam included with Maracaibo balsam in the German Pharmacopœia (D. A. III.). They are equivalent, but the first-named gives a red coloration in the D. A. III. acid test. According to Beckurts and Brüche no such coloration occurs, the balsam behaving in a normal manner.

The opinion of the last-named workers was that the qualitative and quantitative tests indicated an adulterated sample of Angostura balsam.

It is evident from the different results obtained by Beckurts and Brüche, and by Gehe & Co., that variations exist in these products. The results must therefore be

accepted *cum grano salis*, and are of the less importance in that this balsam is now no longer met with in commerce.

The author has examined several Angostura balsams by the methods proposed for Maracaibo balsam (see p. 84), and obtained the following values :—

| | I. | II. | III. |
|---|---|---|---|
| Acid value (direct) . . | 79·52 | 83·00 | 75·87 |
| | 80·70 | 83·50 | 76·32 |
| Ester value . . . . . | 16·24 | 8·36 | 16·07 |
| | 17·38 | 7·94 | 16·19 |
| Saponification value (cold) . | 95·76 | 96·36 | 91·54 |
| | 98·08 | 91·44 | 92·51 |

The acid test of the Pharmacopœia was not tried. That the above values differ from those obtained by Beckurts and Brüche confirms the latter's view that they were working with an adulterated sample.

(*N.B.*—The bibliographical references relating to all the various copaiba balsams will be found on p. 99.)

### 3. Bahia Copaiba Balsam.

Very few analytical data are available on the subject of this variety.

Praël found—sp. gr. 0·980; resin content, 59·80 per cent.; ethereal oil (sp. gr. 0·988), 40·20 per cent.

Umney and Bennett found the specific gravity to be 0·938 and the percentage of essentail oil 49·7.

Beckurts and Brüche found—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . | 73·6 | 97·5 |
| Ester value . . . | *nil* | 15·2 |
| Saponification value (hot) | 73·0 | 112·7 |
| Sp. gr. . . . . | 0·962 | 1·031 (!) |

by the usual method. On the basis of further tests of a qualitative nature, the authors believed both samples to be of questionable purity. As Bahia balsam is now rarely met with in commerce, the above fluctuating values are merely cited without, in the meantime, being credited with any practical importance.

K. Dieterich has also examined Bahia balsam by the same methods as applied to Maracaibo balsam, and obtained the following results :—

I. Balsam of undoubted purity, from the author's own collection—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . | 81·09 | 81·27 |
| Ester value . . . . | 5·08 | 6·08 |
| Saponification value (cold) | 86·17 | 87·32 |

II. An undoubtedly adulterated sample from Hamburg—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . | 64·19 | 64·25 |
| Ester value . . . | 1·76 | 2·60 |
| Saponification value (cold) | 65·95 | 66·85 |

Balsam No. I. was entirely soluble in alcohol, except for a slight turbidity, whilst the No. II. sample was thinner, and only partly soluble, to a turbid solution, in alcohol, numerous large flakes being left behind. The former was undoubtedly pure, but the latter just as certainly adulterated (probably with vaseline oil).

### 4. Carthagena Copaiba Balsam.

For this balsam, Praël found—sp. gr. 0·958; resin content, 46·20 per cent.; ethereal oil (sp. gr. 0·904), 53·80 per cent.

Umney and Bennet give the specific gravity as 0·970 and the essential oil 41·3 per cent.

Kebler found—Oil (b.p. 250°–265° C.), 53 per cent.

Beckurts and Brüche found—

| | |
|---|---|
| Acid value (direct) | 88·9 |
| Ester value | *nil* |
| Saponification value (hot) | 88·9 |
| Sp. gr. | 0·988 |

Gehe & Co. recommend this balsam also as a substitute for Maracaibo balsam, from which, like Angostura balsam, it differs (according to their report) by the positive result (red coloration) given in the D. A. III. acid test.

The author has examined several samples of Carthagena balsam by the method given for Maracaibo balsam and obtained the following values :—

| | I. | II. | III. |
|---|---|---|---|
| Acid value (direct) | 49·00 | 62·30 | 87·75 |
| | 49·40 | 62·76 | 88·23 |
| Ester value | 56·20 | 41·15 | 4·55 |
| | 87·17 | 40·90 | 4·67 |
| Saponification value (cold) | 105·20 | 103·45 | 92·30 |
| | 106·57 | 103·57 | 92·90 |

The sample No. III. agrees well with the figures of Beckurts and Brüche, but Nos. I. and II. seem doubtful products.

### 5. Maracaibo Copaiba Balsam.

This, now officinal, thick balsam has frequently been examined quantitatively.

Praël found — sp. gr. 0·983–0·995; resin, 54·80–61·43 per cent.; ethereal oil (sp. gr. 0·897–0·905), 38·57–45·20 per cent.

According to Keto it has a density of 0·999, acid number 85·4 and ester number 6·7.

Umney and Bennet give the specific gravity as 0·969 and the amount of essential oil 42·5 per cent.

A. Kremel found—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . | 73·0–75·0 | 76·0 |

The ester and saponification values were not determined.

Beckurts and Brüche's figures are as follows :—

| | I. | II. | III. |
|---|---|---|---|
| Acid value (direct) . . | 98·0 | 79·3 | 95·8 |
| Ester value . . . | *nil* | 19·7 | 5·4 |
| Saponification value (hot) . | 98·0 | 99·0 | 100·8 |
| Sp. gr. . . . . | 0·995 | 0·973 | 0·991 |

E. Dieterich found—

| | |
|---|---|
| Acid value (direct) . . . . | 76·52– 94·90 |
| Ester value . . . . . | 0·47– 8·75 |
| Saponification value (hot) . . | 80·27–100·80 |

Solubility in—

| | |
|---|---|
| Ether<br>Chloroform<br>Petroleum ether<br>Oil of turpentine<br>Carbon di-sulphide | complete. |
| Alcohol (90 per cent.)<br>Acetic ether | almost complete |

The usual methods were employed for determining the constants, except that in the saponification test the liquid was concentrated to expel the alcohol, and was then titrated after re-dilution.

L. Maupy proposed to detect ricinus (castor) oil in copaiba balsam by a test based on the fact that when ricinus oil is subjected to dry distillation in presence of caustic potash or soda, the products include sebacic acid and capryl alcohol. The sebacic acid is isolated by decomposing the resulting soap with mineral acids, and is readily soluble in hot water. In testing for ricinus oil, 10 grms. of the suspected copaiba are heated with 10 grms. of dry caustic soda, the ethereal oil being driven off in the form of white

vapours. When ricinus oil is present, a decided odour of capryl alcohol is noticeable. The residue, which, in the meantime, will have separated into an upper wax-like mass and an inferior, liquid stratum, is then stirred with a glass rod, left to cool, treated with 50 grms. of water, heated up, and passed through a wet filter. The sebacic acid separates out from the filtrate, and can be converted into its white lead salt by treating the slightly acid solution in boiling water with lead acetate.

Recently the author has worked out a method for investigating the copaiba balsams, and drawn up a scheme showing the influence exerted by various adulterants on the results.

With normal Maracaibo balsam the following values were obtained—

| | |
|---|---|
| Sp. gr. . . . . | 0·980– 0·990 |
| Acid value (direct) . . . . | 75·0–85·0 |
| Ester value . . . . . | 3·0– 6·0 |
| Saponification value (cold) . . | 80·0–90·0 |

The method adopted for determining these values is carried out as follows :—

(*a*) *Acid value, direct.*—One grm. of balsam is dissolved in 200 c.c. of 96 per cent. alcohol, and titrated with alcoholic $\frac{n}{2}$ potash in presence of phenolphthalein until a red coloration is obtained. The volume of alkali consumed, multiplied by 28·08, gives the acid value.

(*b*) *Saponification value, cold.*—One grm. of balsam is placed in a stoppered 1 litre flask and mixed with 20 c.c. of $\frac{n}{2}$ alcoholic potash and 50 c.c. of benzine (sp. gr. 0·700). After leaving the closed flask for twenty-four hours at room temperature, the contents are diluted with strong alcohol and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The saponification value is obtained by multiplying the volume (c.c.) of combined KHO by 28·08.

(*c*) The *ester value* is found by difference.

The author has examined a number of old and adulterated balsams by this method, and has collected the results into the subjoined table :—

| Copaiba Balsam. | Sp. gr. at 15° C. | Acid Value (direct). | Saponification Value (cold). | Ester Value. |
|---|---|---|---|---|
| Maracaibo D. A. III. (the balsam used in the following adulterations) | 0·985 | 77·31– 78·12 | 80·32– 83·41 | 3·01– 5·29 |
| Maracaibo D. A. III. (3 years old, from the author's collection) | 1·001 | 93·88– 94·33 | 97·56–101·35 | 3·68– 7·02 |
| D.A.III. +10 % Gurjun balsam | 0·987 | 70·20– 71·13 | 76·35– 78·64 | 6·15– 7·51 |
| ,, +20 % ,, ,, | 0·985 | 62·68– 63·90 | 71·56– 71·83 | 7·93– 8·88 |
| ,, +30 % ,, ,, | 0·983 | 55·92– 56·14 | 75·09– 82·03 | 19·13–25·89 |
| ,, +10 % Ordy. olive oil | 0·982 | 71·87– 72·11 | 112·48–113·55 | 40·61–41·44 |
| ,, +20 % ,, ,, | 0·974 | 63·39– 64·66 | 104·74–104·87 | 40·21–41·35 |
| ,, +30 % ,, ,, | 0·967 | 58·46– 58·56 | 122·86–124·80 | 64·40–66·24 |
| ,, +10 % Ricinus (castor) oil | 0·986 | 68·43– 69·89 | 93·79– 97·96 | 25·36–28·07 |
| ,, +20 % ,, ,, | 0·983 | 63·14– 63·32 | 102·94–105·46 | 39·80–42·14 |
| ,, +30 % ,, ,, | 0·980 | 56·80– 58·19 | 114·15–115·95 | 57·35–57·76 |
| ,, +10 % Sassafras oil | 0·994 | 69·98– 70·75 | 75·14– 75·44 | 4·69– 5·16 |
| ,, +20 % ,, ,, | 1·001 | 61·96– 64·13 | 68·40– 68·56 | 4·43– 6·44 |
| ,, +30 % ,, ,, | 1·010 | 55·73– 57·00 | 59·30– 62·14 | 3·57– 5·14 |
| ,, +10 % Oil of turpentine | 0·986 | 69·43– 70·69 | 79·74– 86·64 | 10·31–15·95 |
| ,, +20 % ,, ,, | 0·981 | 63·56– 63·98 | 76·97– 75·75 | 12·19–12·99 |
| ,, +30 % ,, ,, | 0·972 | 56·58– 57·29 | 70·00– 70·77 | 13·42–13·48 |
| ,, +10 % Venice turpentine | 0·992 | 81·14– 82·74 | 85·70– 90·58 | 4·56– 7·84 |
| ,, +20 % ,, ,, | 0·996 | 85·44– 85·76 | 89·76– 90·59 | 4·32– 4·83 |
| ,, +30 % ,, ,, | 0·999 | 88·36– 89·07 | 95·06– 97·80 | 6·70– 8·73 |
| ,, +10 % Colophony . | 0·995 | 85·03– 85·40 | 95·13–102·34 | 10·10–16·94 |
| ,, +20 % ,, | 1·003 | 95·91– 97·47 | 102·65–103·03 | 5·56– 6·74 |
| ,, +30 % ,, | 1·018 | 105·70–106·25 | 110·49–111·17 | 4·79– 4·92 |
| ,, +10 % Liquid paraffin | 0·975 | 68·90– 69·41 | 75·98– 77·09 | 7·08– 7·68 |
| ,, +20 % ,, ,, | 0·963 | 61·41– 62·41 | 70·67– 72·38 | 9·26–10·17 |
| ,, +30 % ,, ,, | 0·951 | 54·55– 56·11 | 78·09– 79·04 | 22·93–23·54 |

Consequently the added adulterants modify the constants of normal Maracaibo balsam in the following manner :—

1. Gurjun balsam lowers acid and saponification values, and raises ester values.

2. Olive oil reduces sp. gr. and acid value, but considerably increases the ester and saponification values.

3. Sassafras oil raises sp. gr., lowers acid and saponification values, leaving ester value almost unchanged.

4. Oil of turpentine reduces sp. gr., acid value, and saponification value, but considerably increases ester value.

5. Venice turpentine increases sp, gr., acid value, and saponification value, leaving ester value almost unchanged.

6. Colophony greatly increases sp. gr., acid and saponification value. No definite conclusions deducible from ester values.

7. Liquid paraffin reduces sp. gr. and acid value, increases ester value, but leaves saponification value nearly normal.

8. Ricinus (castor) oil reduces sp. gr. and acid value, considerably increasing ester and saponification values, like olive oil (No. 2).

9. Resinified old balsam. The acid and saponification values and sp. gr. are greatly increased, analogous to the influence of colophony (No. 6).

Thus, when abnormalities are detected in Maracaibo balsam, an approximate conclusion can be drawn from the above method as to whether the sample is old, resinified, or adulterated, taking the following indications as a guide : —

| The Maracaibo balsam exhibits in comparison with the normal— | Thus foreshadowing the presence of— |
|---|---|
| I. Unduly low acid value.<br>Do. high saponification value.<br>Do. do. ester value. | Gurjun balsam. |
| II. Unduly high sp. gr.<br>Do. acid value.<br>Do. saponification value. | Old, resinified balsam. |
| III. Unduly low sp. gr.<br>Do. do. acid value.<br>Do. high ester value.<br>Do. do. saponification value. | Olive oil or ricinus oil. |
| IV. Unduly low sp. gr.<br>Do. do. acid value.<br>Do. do. saponification value.<br>Do. high ester value. | Oil of turpentine. |
| V. Unduly high sp. gr.<br>Do. acid value.<br>Do. saponification value. | Colophony. |
| VI. Unduly low sp. gr.<br>Do. do. acid value.<br>Do. high ester value. | Liquid paraffin. |
| VII. Unduly high sp. gr.<br>Do. low acid value.<br>Do. do. saponification value. | Sassafras oil. |
| VIII. Unduly high sp. gr.<br>Do. acid value.<br>Do. saponification value. | Venice turpentine. |

The value affording the least guidance is the sp. gr., and for this reason it is highly desirable to fix a relatively small margin of deviation for the sp. gr. of officinal Maracaibo balsam. The author has proposed 0·980–0·990. The values (*e. g.* acid value) obtained by Kremel, E. Dieterich, Beckurts and Brüche can only in part be compared with those of K. Dieterich owing to the differences in the methods employed. Of course the foregoing scheme of differentiating adultera-

tions cannot serve as a guide unless the author's methods of determination be used. The existing method of testing Maracaibo in the German Pharmacopœia, though quantitative, is inaccurate and unsuitable.

As already stated, Gehe & Co. consider the limits of permissive deviation laid down by the author too wide, or as not always permitting the detection of adulterations, they having found that mixtures of Maracaibo and Para balsam with colophony furnish values within the said limits. Gehe & Co. believe—in opposition to the author—that particular value attaches to the Bosetti test, namely, melting the balsam with 30 per cent. of colophony, adding 10 per cent. ammonia, and observing the result as regards gelatinisation, the absence of which phenomenon is considered to indicate purity. The author believes that, as with Peruvian balsam, the accuracy of this assumption cannot be proved until the test has been made with samples of known purity taken direct from the parent tree. At present none of the existing values have been obtained from balsams of unimpeachable purity, so that even the limits given by the author (see also Para balsam), being derived from relatively impure commercial specimens, can only be *à priori* regarded as of relative accuracy. Gehe & Co. state—which is particularly important—that Gurjun balsam is less largely used than thin Para balsam for adulterating Maracaibo balsam.

### 6. Maturin Copaiba Balsam.

Praël found—sp. gr. 0·983; resin, 55 per cent.; ethereal oil (sp. gr. 0·898), 45 per cent.

A. Kremel found the acid value to be 77·1, but did not determine the ester and saponification values.

F. Dietze found, by the usual methods—

| | |
|---|---|
| Acid value (direct) . . . | 78·17 |
| Ester value . . . . | 4·26 |
| Saponification value (hot) . | 82·43 |

He recommended this balsam as a substitute for the officinal variety (Maracaibo), a proposal which seems all the more justifiable in that the characteristic values of the two agree very well, thus differing from the other varieties of copaiba.

The author treated Maturin balsam by the method described on p. 84, and obtained the following results :—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . . . | 78·52 | 82·73 |
| Ester value . . . . . | 12·86 | 9·29 |
| Saponification value (cold) . . | 91·38 | 92·02 |

figures which agree well with those of other workers.

## 7. Gurjun (East Indian) Copaiba Balsam.

This balsam, which is used to adulterate Maracaibo balsam, has been examined by several authors.

A. Kremel found—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Acid value (direct) . . | 20·0 | 19·3 | 14·2 | 5·8 |

by the usual method.

The sp. gr., according to Kebler, at 15° C. is 0·9796; and the ethereal oil (b.p. 254°–263° C.), 54 per cent.

The results of Beckurts and Brüche are as follows :—

| | |
|---|---|
| Acid value (direct) . . . | 8·7 |
| Ester value . . . . | *nil* |
| Saponification value (hot) . | 8·7 |
| Sp gr. . . . . | 0·955 |

E. Dieterich obtained the following results :—

| | |
|---|---|
| Acid value (direct) . . . | 6·5 – 7·4 |
| Ester value . . . . | 10·30–11·20 |
| Saponification value (hot) . | 16·80–18·60 |

Solubility in—

| | |
|---|---|
| Alcohol (90 per cent.) | complete, |
| Chloroform | |
| Acetic ether | |
| Benzol | |
| Oil of turpentine | |
| Ether | incomplete, |
| Petroleum ether | |
| Carbon di-sulphide | |

the usual methods being employed, subject to the same authority's modification, already cited under Maracaibo balsam. More recently the present author has applied the method described on p. 84 to Gurjun balsam, as well as the other varieties of copaiba, and found—

| | |
|---|---|
| Sp. gr. . . . . | 0·955–0·965 |
| Acid value (direct) . . . | 5·0–10·0 |
| Ester value . . . . | 1·0–10·0 |
| Saponification value (cold) . | 10·0–20·0 |

the following values being obtained on a later occasion :—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . . | 10·80 | 10·64 |
| | 10·98 | 10·77 |
| Ester value . . . . | 14·00 | 14·83 |
| | 15·37 | 15·00 |
| Saponification value (cold) . . | 24·80 | 25·47 |
| | 26·35 | 25·77 |

These figures agree with those of Beckurts and Brüche and E. Dieterich, but not with the high acid values found in some cases by Kremel.

To test for Gurjun balsam in copaiba, 4 drops of nitric acid (sp. gr. 1·4) and 1 c.c. glacial acetic acid are poured on the surface, a red zone appears in presence of gurjun.

Gregor and Bamberger found the methoxyl value to be nil.

## 8. Para Copaiba Balsam.

According to Praël the sp. gr. of this balsam is 0·916–0·989; resin, 23·87–59·53 per cent.; ethereal oil (sp. gr. 0·889–0·902), 40·47–76·13 per cent.

Kebler found—sp. gr. 0·9254; oil (b.p. 258°–270° C.), 90 per cent.

According to Umney and Bennett the specific gravity is 0·920, and the amount of oil 62·4 per cent.; while E. Keto found specific gravity 0·92, the acid number 19·4, and the ether number 7·4. Hill and Umney also found sp. gr. 0·896 to 0·910, and optical rotation — 7° to — 35°.

A. Kremel found—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . | 29·6 (!) | 78·2 |

but did not determine the ester and saponification values. The low acid value of No. 1 is abnormal, and Kremel himself considered it questionable.

Beckurts and Brüche found—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . . | 87·0 | 38·1 (!) |
| Ester value . . . . | 0·0 | 2·9 (!) |
| Saponification value (hot) . . | 87·0 | 41·0 (!) |
| Sp. gr. . . . . | 0·984 | 0·949 |

The values marked (!) were regarded by the authors themselves as unusual, and probably attributable to adulterations in the sample.

E. Dieterich found, by the method adopted for Maracaibo balsam—

| | |
|---|---|
| Acid value (direct) | 29·40–65·80 |
| Ester value | 1·90 |
| Saponification value (hot) | 31·30–67·70 |

Solubility in—

| | |
|---|---|
| Ether, Chloroform, Benzol, Oil of turpentine | complete. |
| Alcohol (90 per cent.), Acetic ether, Petroleum ether, Carbon di-sulphide | almost complete. |

K. Dieterich's results are as follows :—

| | |
|---|---|
| Sp. gr. | 0·95– 0·97 |
| Acid value (direct) | 40·0 –60·0 |
| Ester value | 2·0 – 8·0 |
| Saponification value (cold) | 30·0 –60·0 |

and subsequently—

| | I. | II. |
|---|---|---|
| Acid value (direct) | 49·47<br>49·92 | 61·62<br>61·86 |
| Ester value | 15·15<br>18·06 | 9·06<br>8·89 |
| Saponification value (cold) | 64·62<br>67·98 | 70·68<br>70·75 |

Apart from the somewhat higher ester value, these figures correspond fairly well with the others given above.

These last-named values were obtained by the author's own method, already described. He proposed to constitute the first set a standard for good Para balsam, but, according to Gehe & Co., this is inadmissible.

The author has, in this case also, examined the influence of adulterants on the normal values :—

| Copaiba Balsam. | Sp. gr. | Acid Value (direct). | Sapon Value | Ester Value. |
|---|---|---|---|---|
| Para +10 % Gurjun balsam . | 0·971 | 41·59–43·27 | 62·54– 70·13 | 20·95–26·86 |
| ,, +20 % ,, ,, | 0·974 | 38·13–38·97 | 73·33– 74·93 | 35·20–35·96 |
| ,, +30 % ,, ,, | 0·974 | 34·25–34·30 | 71·85– 71·94 | 37·60–37·64 |
| ,, +10 % Olive oil (ordy.) | 0·971 | 41·36–46·02 | 86·26– 89·85 | 43·83–44·90 |
| ,, +20 % ,, ,, | 0·964 | 37·40–38·22 | 90·89– 97·85 | 53·49–59·63 |
| ,, +30 % ,, ,, | 0·955 | 35·44–37·05 | 102·40–103·26 | 66·21–66·96 |
| ,, +10 % Ricinus (castor) oil | 0·972 | 40·83–41·34 | 93·45– 94·54 | 52·62–53·20 |
| ,, +20 % ,, ,, | 0·970 | 37·55–38·07 | 89·28– 92·33 | 51·73–54·26 |
| ,, +30 % ,, ,, | 0·966 | 38·89–38·97 | 97·01– 97·95 | 58·12–58·98 |
| ,, +10 % Sassafras oil . . | 0·985 | 45·45–45·98 | 53·67– 54·44 | 8·22– 8·46 |
| ,, +20 % ,, ,, | 0·985 | 43·84–44·90 | 47·31– 47·98 | 3·08– 3·47 |
| ,, +30 % ,, ,, | 0·995 | 39·83–40·29 | 44·81– 46·65 | 4·98– 6·36 |
| ,, +10 % Oil of turpentine | 0·973 | 42·44–42·97 | 70·26– 75·04 | 27·82–32·07 |
| ,, +20 % ,, ,, | 0·969 | 41·18–41·33 | 59·01– 59·04 | 17·71–17·83 |
| ,, +30 % ,, ,, | 0·960 | 39·76–40·12 | 51·10– 52·45 | 11·34–12·33 |
| ,, +10 % Venice turpentine | 0·980 | 53·69–54·14 | 70·99– 71·17 | 17·03–17·30 |
| ,, +20 % ,, ,, | 0·982 | 62·82–63·18 | 72·17– 75·96 | 9·35–12·78 |
| ,, +30 % ,, ,, | 0·986 | 68·99–69·02 | 81·81– 82·99 | 12·82–13·97 |
| ,, +10 % Colophony . . | 0·982 | 57·92–60·16 | 68·92– 70·98 | 10·82–11·00 |
| ,, +20 % ,, | 0·991 | 75·56–75·72 | 89·80– 91·21 | 14·24–15·49 |
| ,, +30 % ,, | 1·000 | 90·33–91·67 | 93·13– 94·12 | 2·45– 2·80 |
| ,, +10 % Liquid paraffin . | 0·962 | 39·95–41·68 | 66·83– 68·49 | 26·81–26·88 |
| ,, +20 % ,, ,, | 0·951 | 33·86–34·09 | 55·35– 57·66 | 21·49–23·57 |
| ,, +30 % ,, ,, | 0·935 | 30·79–31·11 | 51·89– 53·46 | 21·10–22·35 |

The effects of adulterants on normal Para balsam may be summarised as follows :—

1. Gurjun balsam increases the sp. gr., reduces the acid value, and considerably raises the saponification and ester values.

2. Olive oil, ricinus oil, and other fatty oils lower the sp. gr. and acid value, but considerably increase the saponification and ester values.

3. Sassafras oil raises the sp. gr., but depresses the acid and saponification values.

4. Oil of turpentine lowers the sp. gr. and acid value, but largely increases the ester value.

5. Venice turpentine raises the sp. gr. and the acid, ester, and saponification values.

6. Colophony raises the sp. gr., acid value, and saponification value.

7. Liquid paraffin reduces the sp. gr., greatly lowers the acid and saponification value, but raises the ester value.

In the case of abnormal values furnished by Para balsam, the author's method affords a means of forming a relatively accurate opinion as to whether the sample is old, resinified, adulterated, or altered in some other way. The following indications will serve as a guide :—

| When Para balsam exhibits the following abnormalities :— | The presence of the subjoined bodies may be presumed— |
|---|---|
| I. Unduly high sp. gr.<br>Do. low acid value.<br>Do. high saponification value (cold).<br>Very high ester value. | Gurjun balsam. |
| II. Unduly low sp. gr.<br>Do. acid value.<br>Very high ester value.<br>Do. saponification value. | Olive oil, ricinus oil, and fatty oils generally. |
| III. Unduly high sp. gr.<br>Do. low acid value.<br>Do. do. saponification value. | Sassafras oil. |
| IV. Unduly low sp. gr.<br>Do. acid value.<br>Very high ester value. | Oil of turpentine. |
| V. Unduly high sp. gr.<br>Do. acid value.<br>Do. ester value.<br>Do. saponification value. | Venice turpentine. |
| VI. Unduly high sp. gr.<br>Do. acid value.<br>Do. saponification value. | Colophony. |
| VII. Unduly low sp. gr.<br>Very low acid value.<br>Do. high ester value. | Liquid paraffin. |

With regard to sp. gr., the remarks already passed on Maracaibo balsam also apply here.

### 9. Surinam Copaiba Balsam.

**Origin.**—*Copaïfera guianensis* and other Copaïferæ.

**Habitat.**—Surinam.

**Chemical Constituents.**—Copaibic acid, ethereal oil, 78 per cent. (Pool).

**General Properties and Commercial Varieties.**—The balsam is a clear, pale yellow, non-opalescent liquid, resembling olive oil, and miscible in all proportions with ether, chloroform, petroleum ether, and carbon di-sulphide. In Surinam the balsam is known as "hoopal" or "hooper" oil, on account of the wood being used for hooping sugar casks. This balsam is seldom met with in commerce.

**Adulterants.**—Other balsams.

**Analysis.**—Pool investigated this balsam, with the following results :—

The sp. gr. is 0·942, and the balsam is miscible with petroleum ether, chloroform, ether, and carbon di-sulphide in all proportions. Mixed in equal proportion with alcohol it remains turbid, but dissolves when the alcohol is increased four or five fold. The (hot) saponification value is 34. One and a half grm. of balsam combines with 94 mgrms. of iodine, the iodine value is therefore 6·27. The balsam contains 78 per cent. of a colourless ethereal oil of sp. gr. 0·94 and B.P. 250°–260° C. The residual resin left after distilling off this oil was extracted with dilute alcohol, the evaporated extract leaving crystals of copaibic acid of M.P. 130° C. It differs from the ordinary thick commercial balsam by its solubility in petroleum ether. On shaking up the carbon di-sulphide solution with a mixture of equal parts sulphuric acid and nitric acid, the latter turns brown, but the former does not assume a violet tint. When mixed with one-third

volume of ammonia, a clear solution is produced. Bromine in twenty parts of chloroform gives a violet coloration with the balsam. Lead acetate gives no turbidity or precipitate. The ethereal oil gives a pure red coloration with bromine-chloroform mixture, a brown-red with concentrated sulphuric acid, and a green with chloral hydrate on heating.

A sample of Copaiba balsam from Surinam has been examined by L. van Itallie and C. H. Nieuwland, who found that for the most part it was soluble in a 5 per cent. aqueous solution of sodium carbonate. The resin acid separated from the solution was amorphous, but appeared to be nearly a pure substance, acid number 171·7, saponification number 178. The resene was also amorphous. The sesquiterpene alcohol which exists in the balsam had a M.P. of 114°–115°, and yielded a sesquiterpene having the formula $C_{15}H_{24}$, B.P. 252°, sp. gr. 0·952 at 15°, a refractive index at 15°, 1·5189, and specific rotation $[a]_D$ — 61·7°. In contact with the air this terpene soon changed to a resinous solid.

**Maranham Copaiba Balsam.**—Umney and Bennett found the sp. gr. of this variety to be 0·990, and the amount of ethereal oil 41·8 per cent.

A sample of Copaiba balsam from Amazonas, Brazil, was found by J. D. Riedel to have the following characters :— It was a pale yellow non-fluorescent fluid having the usual odour and flavour ; with an equal volume of absolute alcohol it yielded a turbid liquid, and on further addition of alcohol there was a white precipitate. The sp. gr. at 15° was 0·930, acid value 8·3, ester value 23·8, and saponification value 42·1. The rotation was — 40°. It yielded 20·4 per cent. of resin, with a rotation at 20° of — 55°, and the essential oil had a rotation at 20° of — 35° 20′.

Bolivian Copaiba balsam was found by Hartwich to have a density at 15°, 0·998 ; $[a]_D$ at 15° + 36°, refractive index at 20°, 1·522, acid number (indirect) 89·7, saponification

number (cold), 97·25. It yielded on distillation 23 per cent. of a volatile oil having a density at 15°, 0·916, $[a]_D + 18°$, refractive index at 20°, 1·5048; 70 per cent. of this oil distilled between 250° and 270°, and probably contained cadinene and caryophyllene.

Surinam balsam is distinguished from Maracaibo balsam by the blue colour which an acetic anhydride solution yields with sulphuric acid.

## 10. West African (Illurin) Copaiba Balsam.

This is a brownish material showing a greenish fluorescence.

Tschirch states that a West African Copaiba balsam, obtainable in the London market, gives the same reactions as Maracaibo balsam. Umney has also examined this balsam, and is inclined to attribute it to *Hardwickia Manii*. Several kinds have also been investigated by Peinemann (*Ap. Ztg.*, 1884, pp. 8 *et seq.*), especially as regards their constituent oils.

Gehe & Co. found—

| | |
|---|---|
| Sp. gr. . . . . | 0·990 |
| Acid value (direct) . . | 57·60 |
| Residual resin . . . | 56 per cent. |

The balsam is thick, and of dark brown colour; solidifies with ammonia, but gives no colour reaction under the D. A. III. test, thus behaving like true balsams.

Keto gives the following results:—

| | |
|---|---|
| Sp. gr. . . . . | 0·9905 |
| Acid number . . . | 55·5 |
| Ether number . . . | 8·3 |

Umney obtained from African balsam 30 per cent. of an oil having a sp. gr. of 0·918 and a rotation of + 20° 40′.

The author examined Illurin balsam by the method described on p. 84, and obtained the following values :—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . . | 58·74 | 59·33 |
| Ester value . . . . | 9·62 | 9·62 |
| Saponification value (cold) . . | 68·36 | 68·95 |

which agree with those obtained by Gehe & Co., and approximate Illurin balsam more nearly to Para balsam than to Maracaibo balsam.

According to Caesar and Loretz the addition of African or Illurin balsam to Copaiba balsam may be detected by an examination of the oil obtained by distilling the balsam in a current of steam.

They found that pure balsams were dextrorotatory, but yielded a lævorotatory oil and a dextrorotatory resin ; on the other hand, African balsam yielded a dextrorotatory oil and a lævorotatory resin.

A considerable number of Copaiba balsams have been examined by Messrs. Evans' Sons, Lescher, and Webb, the results being tabulated in their annual *Analytical Notes*. The results are far too numerous to reproduce here, but a short summary of the figures obtained, with presumably pure balsams, may be found useful; for the full details see the above.

| | Balsams. | | Refractive Index. | Acid Value of Resin. | Volatile Oils. | | |
|---|---|---|---|---|---|---|---|
| | P.c. of Essential Oil. | Acid Value. | | | Sp. gr. | Optical Rotation. | Refractive Index. |
| Maranham . | 36 to 56 | 63 to 89·6 | 1·5098 to 1·5168 | 120·8 to 172·0 | 0·896 to 0·904 | − 1° 30′ to − 21° 42′ | 1·4946 to 1·4995 |
| Maracaibo . | 44 to 46 | 79·1 to 91·4 | 1·5136 to 1·5183 | 143 to 170 | 0·897 to 0·903 | − 6° 0′ to − 10° 0′ | 1·4975 to 1·4988 |
| Maturin . | 40 | 91 | Sp. gr. 0·997 | 151·7 | 0·912 | − 0° 48′ | — |
| Para . . | 42 to 77·5 | 21 to 72·1 | 1·4992 to 1·515 | 70 to 163 | 0·866 to 0·908 | − 14° 28′ to − 33° 14′ | 1·4935 to 1·5026 |
| Carthagena . | 40 to 50 | — | — | — | 0·894 to 0·910 | − 40° 0′ to + 0° 30′ | — |
| Bahia . . | 44 to 64 | 42 to 56 | 1·507 to 1·5124 | 106 to 155·5 | 0·893 to 0·909 | − 2° 42′ to − 28° | 1·492 to 1·4952 |
| African . . | 48 | — | — | — | 0·920 | + 16° | — |
| Gurjun . . | 50 | 7·5 | — | — | 0·9244 to 0·964 | − 10° to + 78° 30′ | 1·5024 to 1·5113 |

The presence of African balsam in Copaiba balsam may readily be detected by examination of the volatile oil, as shown by the following results given by J. C. Umney :—

| | African Balsam. | Maracaibo Balsam. | Para Balsam. |
|---|---|---|---|
| Percentage of oil in balsam | 32 | 42 | 64·3–80·2 |
| Sp. gr. of oil at 15° | 0·9180 | 0·9050 | 0·9060 |
| Rotation in 200 mm. tube | + 20·7° | − 34·3° | − 28·9° |
| Solubility in absolute alcohol at 15° | Not sol. in 50 vols. | Sol. in equal vol. | Sol. in equal vol. |
| Boiling-point range | 260°–273° | 245°–265° | 252°–260° |

**Resin of Daniella Thurifera.**—West African or Illurin balsam is the product of *Daniella thurifera*, but the tree also yields a resin which exudes in a liquid state through the bark and then dries; it is sometimes found at the foot of the tree. Four samples of this resin have been examined at the Imperial Institute, three of these being from Northern Nigeria and one from the Gambia. The results are given below :—

| | Northern Nigeria. | | | Gambia. |
|---|---|---|---|---|
| | From tree. | From tree. | From the ground. | "Incense Resin." |
| Ash | Trace | 1·2 % | 0·35 % | 0·32 % |
| Acid number | 97 | 132 | 105 | 109 |
| Melting-point (C.) | 90° (approx.) | 90° (approx.) | 110°–115° | 110°–115° |

The resins dissolve completely, or almost completely, in turpentine and in alcohol. *B. Dalzielli*, *B. odorata*, and *B. floribunda* (Royle) also yield odoriferous resins.

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## 11. Mecca Balsam.

*Balsamum de Mecca.*

**Origin and Habitat.**—*Balsamodendron Gileadense; Commiphora opobalsamum.* Arabia.

**Chemical Constituents.**—Ethereal oil, 10 per cent.; soluble agglutinant resin, 70 per cent.; insoluble resin (burserin), 12 per cent.; bitter extract, 4 per cent.; acid matter and foreign admixtures, 1 per cent. (Bonastre); bitter principles and resenes (Baur).

**General Properties and Commercial Varieties.**—The balsam varies, according to age, from a pale, thin liquid to thick, dark yellow or brown, with a very agreeable aromatic odour when fresh, but with an odour of turpentine when aged.

In Bombay this Gilead balsam is known as "Balsan-Katel," and is imported from Arabia, under the name of "Duhnul-balasan." The wood of the balsam tree (*Balsamodendron opobalsamum*) is known in India by the name "Xylobalsamum," the fruit as "Carpobalsamum."

**Adulterants.**—Turpentine and artificial preparations of resin and oil of turpentine.

**Analysis.**—The published data are very scanty.

Hirschsohn found that several of the samples—of unknown purity—examined by him formed clear solutions in alcohol-ether, and also in petroleum ether.

A. Kremel found—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . | 45·1 | 51·8 |

E. Dieterich found—

| | |
|---|---|
| Acid value (direct) . . | 40·10–94·08 (!) |

Solubility in—

| | |
|---|---|
| Ether, Chloroform, Acetic ether, Benzol | complete. |
| Alcohol (90 per cent.), Petroleum ether, Oil of turpentine, Carbon di-sulphide | almost complete. |

According to Sawer, the pure balsam is at first turbid and white, with a strong, agreeable odour, and bitter, astringent taste. After a short time the balsam becomes thin, with a greenish sheen, then golden yellow, and finally the colour of honey. A single drop let fall into water sinks to the bottom, then rises to the top again, where it spreads out in a cloudy film, which rapidly hardens, owing to the evaporation of the ethereal oil, and can then be taken out of the liquid. According to Guibourt, the balsam in ageing turns brown and thick, and, as a result of the volatilisation of the ethereal oil, is no longer able to reascend and spread out when dropped into water. When rubbed in the hand, the balsam loses its ethereal oil, and becomes solid. When

rubbed on paper, it makes no greasy mark; and it does not harden with calcined magnesia. On mixing 5 grms. of balsam with 30 grms. of 90 per cent. alcohol, a milky liquid is produced, which in eight to ten days deposits a mucinous sediment and becomes translucent.

According to Baur, this balsam is soluble in ether, ether-alcohol, acetone, and acetic acid, but forms merely a turbid solution with alcohol, petroleum ether, benzol, chloroform, toluol, and carbon di-sulphide, a brownish yellow superficial layer separating out from the last-named solvent.

The author has applied the method described on p. 70 to several specimens of Mecca balsam, one of them (I.) being fresh, and another (II.) old and resinified. The following values were obtained :—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . . | 39·84 | 60·77 |
| | 39·96 | 61·37 |
| Ester value . . . . | 101·10 | 81·90 |
| | 101·39 | 82·66 |
| Sapon. value (cold) . . | 140·94 | 142·67 |
| | 141·35 | 144·03 |

The fresh, pure balsam had a very pale colour, highly agreeable aromatic odour, and lower sp. gr. than when old, the latter having a very disagreeable smell of turpentine, and being dark brown in colour and very viscid. As in the case of Copaiba balsam, the acid value increases as resinification progresses. The high acid values (up to 90) obtained by E. Dieterich probably refer to old samples.

Wiesner avers that when pure Mecca balsam is rubbed down with potato starch and examined under the microscope, the extreme outer contour of the starch granules alone remains visible, *i. e.* Mecca balsam has the same refractive power as starch. As soon, however, as an addition of fatty oil (6 per cent. and upwards) is made, the starch granules

become well defined; a test enabling adulteration with such oils to be detected.

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## 12. Peruvian Balsam.

*Balsamum de Peru* (officinal in German Pharmacopœia).

**Origin and Habitat.**—*Myroxylon Pereiræ* (Papilionaceæ). Western Central America.

**Chemical Constituents.**—Cinnamëin, consisting mainly of the benzyl ester of benzoic acid ($C_7H_5O_2 . C_7H_7$, B.P. 303°–304°), with a smaller proportion of the benzyl ester of cinnamic acid ($C_9H_7O_2 . C_7H_7$), free cinnamic acid, vanillin, and the peruresinotannol esters of cinnamic and benzoic acids. The isolated peruresinotannol has the formula $C_{18}H_{20}O_5$ (Trog), $C_{18}H_{19}O_4$ (Tschirch), also a substance resembling a phytosterol, M.P. 80° (Thoms), and traces of styrol, stilbene, and vanillin.

According to the latest researches, cinnamëin is principally composed of esters of benzoic and cinnamic acids, with benzyl alcohol ($C_7H_8O$, B.P. 200°) and a new alcohol, peruviol ($C_{13}H_{22}O$), which has an odour of honey. Cinnamic alcohol has not been detected, but di-hydrobenzoic acid is probable. The ratio of cinnamic acid to benzoic acid is about 40 : 60. Iso- and allo-cinnamic acid were not detected (Thoms).

The myroxocarpin ($C_{48}H_{35}O_6$) formerly observed in white Peruvian balsam (as at one time met with in commerce), but

afterwards unsuccessfully sought for, has again been found by Tschirch.

Whereas the cinnamëin examined by Thoms consisted for the most part of cinnamic benzyl ester with only a little benzoic benzyl ester, the Peruvian balsam (*i. e.* the cinnamëin isolated therefrom) examined by Tschirch showed a converse ratio. Tschirch believes this variation to be due to irregularities in the method of collecting the balsam. (This point has already been referred to by the present author, on the basis of the irregular analytical results obtained by him.)

**Analysis.**—Caesar & Loretz made the following remarks in their report, dated October 1899 :—" According to the researches of Fromme, it is necessary to the attainment of concordant results in the determination of cinnamëin by parallel analyses that the amount of water employed for agitation should be strictly regulated, and—like the quantity of soda used—kept down to a minimum, since otherwise a not unimportant percentage of cinnamëin is retained in the liquid. Particularly concordant values were obtained by Fromme, by using first 25 c.c., then 5 c.c. of 2 per cent. caustic soda, and then 2 × 5 c.c. of water for the agitation.

" In the present state of our knowledge of the balsams, the following points seem to us of importance in the testing of Peruvian balsam :—

" 1. Limiting the sp. gr. to 1·136–1·150.

" 2. The nitric acid test with benzol-free benzine, in presence of five drops of $HNO_3$ (sp. gr. 1·38). The coloration of the entire mass when the reaction has set in should be yellow to brownish yellow.[1]

[1] In the author's opinion, it is a pity that prominence should be again given to this unreliable test in face of the really useful quantitative tests. In view of the failure of this nitric acid reaction with the pure drug, the

"3. The cinnamëin determination by the Thoms method, with the foregoing slight modification, should yield at least 90 per cent.

"4. The identification of the cinnamëin by the ester value, which should be under 235."

The composition of *white* Peruvian balsam has not yet been closely studied, the samples to be found in existing collections differing considerably from one another, so that no precise conclusions can be drawn. At all events, according to Germann, the product obtained from the fruit of *Myroxylon Pereirae* differs in composition from the white Peruvian balsam examined by him. Guibourt classes the white (Indian) balsam as identical with the American storax from *Liquidamber styraciflua* (see Storax).

**General Properties and Commercial Varieties.**—At the present time the white variety from the fruit of *Myroxylon Pereirae* is no longer met with in commerce, the *black* balsam alone being now listed. This latter kind forms a thick, brownish black balsam, transparent in thin layers, the odour of which is very agreeable and aromatic, and the flavour irritating, hot and bitter: sp. gr. 1·137–1·150 at 25° C. It is almost completely soluble in alcohol, chloroform, glacial acetic acid, and acetic ether, but only partly soluble in other inert solvents.

The balsam recovered by boiling the bark—Balsamo de Cascara or Tacuasonte—is of inferior quality. A balsam similar to the officinal preparation, derived from *Myrocarpus frondosus*, is no longer in commerce.

**Adulterants, etc.**—Ricinus oil, olive oil, and fatty oils generally, Copaiba balsam, Gurjun balsam, colophony, turpentine, and Tolu balsam.

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only course that can be advised is to omit it altogether, more especially since the efficacy of the quantitative reactions already given in the present work is obvious.

**Analysis**.—Like Copaiba, Peruvian balsam has been widely and thoroughly investigated. Unfortunately, all the trouble taken has proved unavailing, the au'hor having shown by means of sundry samples of undoubtedly pure balsam from Honduras, taken direct from the parent tree, that all the commercial qualities of Peruvian balsam are adulterated, and that quantitative tests alone are capable of determining the value of this balsam, qualitative tests never. This explains the extraordinary divergence in the reports furnished by various workers, each of whom had different samples of the balsam, all adulterated, as the subject of their qualitative tests.

Recently, specimens of San Salvador balsam, taken direct from the tree, were examined by Thoms, who characterises the quantitative method as the only accurate one. Of the authors who formerly occupied themselves in devising and applying qualitative reactions that are no longer suitable—such as the lime and petroleum ether tests, as well as those given in the German Pharmacopœia—the following may be mentioned :—Ulex, Grote, Evan, Nietsche, Schweickert, Oberdörffer, Vulpius, Musset, Gehe & Co., Caesar & Loretz, Hirschsohn, Kinzel, Schade, Wimmel, Denner, and others.

The first quantitative method—determination of cinnamëin, styracin, etc.—was published in a large and comprehensive treatise by Andrée. The same method was afterwards practised by Kremel, who, in addition, made determinations of the acid, ester, and saponification values. Gehe & Co. immediately evinced great foresight in rightly characterising these quantitative methods as a valuable progressive step.

The estimation of cinnamëin was subsequently recommended by Kinzel, without any reference to the previously

published labours of Andrée and Kremel. Thoms then raised objection to the methods given in the German Pharmacopœia for the determination of the acid, ester, and saponification values, by rightly laying emphasis on the existing excessive fluctuations. The sp. gr. was reported upon by Wimmel (extreme limits, 1·138 and 1·148; general range, 1·140–1·145), and also by Vulpius and Schlickum. Musset worked out a quantitative method, analogous to that of E. Dieterich by determining the portions soluble in benzine and alcohol; Denner communicated new cholesterin reactions and a quantitative method based on the behaviour of the alkaline-earth compounds of the various constituents. (More recently the cholesterin reactions of the resins and their constituents have again been investigated by Tschirch.) By means of authentic unadulterated specimens of Honduras balsam the author has been able to show that the tests prescribed by the German Pharmacopœia are entirely erroneous. He finds that—

1. The perfectly pure balsam hardens with calcium hydrate, although the Pharmacopœia states that it should not harden.

2. When rubbed down with sulphuric acid and washed, the pure balsam does not furnish a hard mass—as required by the Pharmacopœia (D. A. III.)—but gives an almost greasy mass.

3. The test prescribed for the detection of Gurjun balsam (bluish green coloration after extraction with benzine and treatment with $HNO_3$) is in reality characteristic of the pure balsam, and therefore entirely useless for the purpose specified.

4. Carbon di-sulphide extracts from the pure balsam certain constituents which strongly colour the solvent. Hence the requirement of the German Pharmacopœia that

the balsam should only slightly stain the carbon di-sulphide, and not turn the same brown, is in no way justified, nor does it furnish any conclusion as to the purity of the balsam.

Consequently the foregoing qualitative reactions are devoid of any value, and it is not astonishing that various authors experimenting with these methods have arrived at divergent results, or that increasing difficulty has been experienced in finding specimens that would pass the tests, even the most skilful adulterators having apparently failed.

In view of the variable composition of the product, it is scarcely a matter for surprise that the first values obtained by the use of quantitative tests were very irregular. Which of these values should be regarded as approximately normal was first shown by the author, with pure and unadulterated balsams, and later by Thoms with pure Salvador balsams.

The colour reactions with hydrochloric chloral hydrate, recently communicated by Mauch, for the detection of adulterants in Peruvian balsam may be mentioned without assigning them greater value than to colour reactions in general. The Mauch chloral hydrate method may well be useful for detecting ricinus oil (which is sparingly soluble in 60 per cent. chloral hydrate solution); treated in this way a balsam adulterated with 8 per cent. of ricinus oil gives a turbid mixture, whereas pure Peruvian balsam is soluble to a clear solution in five parts of a 60 per cent. solution of chloral hydrate. In the Ph. G. V. test 1 grm. of Peru balsam should be entirely soluble in 3 grms. of chloral hydrate and 2 grms. of water.

Kremel was the first to determine the acid, ester, and saponification values, and the percentages and saponification value of the contained cinnamëin and resin esters, the cinnamëin estimation being performed by the Andrée method.

The results of Kremel are given below :—

| | | I. | II. | III. |
|---|---|---|---|---|
| Balsam | Acid value (direct) | 40·4 | 40·4 | 49·4 |
| | Ester value | 187·8 | 199·2 | 181·1 |
| | Saponification value (hot) | 228·2 | 239·6 | 230·5 |

| | | I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Per cent. of Cinnamëin | | 68·75 | 67·53 | 66·65 | 77·53 |
| Do. | Resin esters | 29·94 | 32·31 | 32·95 | 21·58 |
| Cinnamëin | Acid value (direct) | 20·3 | 23·4 | 37·9 | 28·3 |
| | Ester value | 214·7 | 207·0 | 202·0 | 68·5 |
| | Sapon. value (hot) | 235·0 | 230·4 | 239·9 | 96·8 |

| | | I. | II. | III. |
|---|---|---|---|---|
| Resin esters | Acid value (direct) | 93·0 | 82·4 | 71·4 |
| | Ester value | 128·8 | 110·4 | 116·4 |
| | Saponification value (hot) | 221·8 | 192·8 | 187·8 |

The following values were obtained by E. Dieterich :—

| | |
|---|---|
| Acid value (direct) | 30·80– 61·60 |
| Ester value | 159·60–223·60 |
| Saponification value (hot) | 221·20–254·80 |
| Sp. gr. | 1·139 |

Solubility in—

Chloroform, Acetic ether } complete.

| | | |
|---|---|---|
| Alcohol (90 per cent.) | 99·74 per cent. | soluble. |
| Ether | 93·77–97·60 | ,, ,, |
| Benzol | 94·27–98·03 | ,, ,, |
| Petroleum ether | 66·04–67·93 | ,, ,, |
| Oil of turpentine | 85·83–88·86 | ,, ,, |
| Carbon di-sulphide | 86·16–87·66 | ,, ,, |

The following figures for commercial samples of Peruvian balsam have been recorded by Evans and others :—

| | |
|---|---|
| Specific gravity | 1·137–1·1665 |
| Refractive index at 15° | 1·585–1·5983 |
| Acid value | 56–80 |
| Saponification value | 212·3–280 |
| Iodine value | 38–54·7 |

| | |
|---|---|
| Percentage of cinnamëin . . . . | 56·0–62 |
| Specific gravity of cinnamëin . . . | 1·0965–1·1054 |
| Refractive index at 15° . . . . | 1·575–1·579 |
| Saponification value . . . . | 233·5–244·2 |
| Iodine value . . . . . | 21·5–25·5 |

Evans' draws attention to the difficulty of determining the purity of this drug by analytical means, and quotes in support of this statement the three analyses reproduced below :—

| | Most Reliable Commercial Natural Balsam. | Cheaper so-called Genuine Balsam, but Synthetic. | Mixed Artificial and Natural Balsam. |
|---|---|---|---|
| Acid value . . . . . | 74·2 | 61·1 | 60·2 |
| Saponification value (hot) . . | 233 | 235 | 222 |
| Iodine value . . . . . | 42·7 | 37·5 | 44 |
| Refractive index . . . . | 1·590 | 1·586 | 1·586 |
| Cinnamëin, per cent. . . . | 57–60 (liquid) | 57–60 (liquid) | 80–85 (semi-solid) |
| Saponification value of ditto . | 238 | 233 | 206 |
| Dieterich's test . . . . . | Doubtful | Doubtful | Reacts, but not decisively |
| Caesar's test (nitric acid) . . | Transient violet, changing to yellow-green | Doubtful, changes to yellow-green | Transient violet, changes to green, probably due to Gurjun balsam |

A sample of white Peru balsam from Honduras has been examined by C. Hartwich and A. Hellström. This was a turbid, yellow, syrupy liquid, sp. gr. 1·089, refractive index at 20°, 1·5925, optical rotation at 20° $[a]_D + 7° 20'$. The acid number was 27 and the saponification number 165. The solubility in alcohol was 94 per cent. and the content of cinnamëin 75 per cent. The portion insoluble in alcohol was found to contain honduresen ($C_6H_{64}O_{10}$, M.P. 310°–315°), and from the portion soluble in alcohol the following constituents were isolated :—honduresinol ($C_{16}H_{26}O_2$, M.P.

286°), cinnamic acid, a resinol, apparently identical with styresinol ($C_{16}H_{26}O_2$, M.P. 156°–161°), honduresinotannol ($C_{40}H_{45}O_{10}$, softening point 300°), and after hydrolysing with concentrated caustic soda solution, cinnamic alcohol, phenylpropyl alcohol. The portion volatile in steam consisted of phenylpropyl alcohol and a terpene ($C_{10}H_{16}$, B.P. 261°–262°).

Five samples of Honduras balsam have been examined by Tschirch and Werdmüller. These had an odour of storax, and yielded the results given below :—

| | | | | Dark-coloured. | |
|---|---|---|---|---|---|
| | 1. | 2. | 3. | 4. | 5. |
| Specific gravity . . . | 1·0886 | 1·0905 | 1·0884 | 1·0897 | 1·0915 |
| Acid value (average) . . | — | 32·67 | — | — | 29·9 |
| Saponification value . . | — | 173·2 | — | — | 153·9 |
| Free acid calc. as cinnamic | — | 8·64% | — | — | — |
| Total acid „ „ | — | 45·66% | — | — | — |

The balsam contained in addition honduresinol ($C_{16}H_{26}O_2$, M.P. 166°–167°) and $\beta$-honduresene ($C_{38}H_{38}O_4$, M.P. 300°). The "cinnamëin" was found to contain a hydrocarbon-hondurane ($C_8H_{10}$, B.P. 154°–155°) and the cinnamic esters of cinnamyl alcohol, phenylpropyl alcohol, and a third alcohol-hondurol ($C_{17}H_{16}O_2$, M.P. 42·5°).

The author has made extensive researches with Peruvian balsam, and adopted the following method of examination:—

(*a*) *Acid value* (direct)—

One grm. of the balsam is dissolved in 200 c.c. of 96 per cent. alcohol and titrated with alcoholic $\frac{n}{10}$ potash, with phenolphthalein as indicator. The acid value is calculated by multiplying the volume of consumed alkali by 5·616.

(*b*) *Saponification value* (cold)—

One grm. of the balsam is weighed into a 500 c.c. stoppered glass flask and left in contact with 50 c.c. of benzine (sp. gr. 0·700) and 50 c.c. of alcoholic $\frac{n}{2}$ potash for twenty-four hours at room temperature, the flask being kept well closed, and shaken up at frequent intervals; 300 c.c. of water are then added, the whole shaken up to dissolve the deposited dark potash salts, and titrated with $\frac{n}{2}$ sulphuric acid and phenolphthalein, with constant agitation. The volume (c.c.) of potash combined, multiplied by 28·08, gives the saponification value (cold).

(*c*) *Ester value*—

This is obtained by subtracting the results of (*a*) from those of (*b*).

(*d*) *Portion insoluble in ether*—

To determine this portion quantitatively, 1 grm. of the balsam is warmed with ether in a small beaker, and extracted on a tared filter until the ethereal filtrate ceases to exhibit colour or leave any residue, when a single drop is tested by evaporation on a watch glass. The residue on the filter is dried at 100° C., weighed, and calculated in percentages.

(*e*) *Determination of the aromatic and volatile constituents* (cinnamëin, etc.)—

The practical performance of the cinnamëin estimation follows on after the preceding determination, the ethereal solution from (*d*) being shaken up with 20 c.c. of 2 per cent. caustic soda in a separating funnel and carefully separated, a single agitation being quite sufficient to dissolve the resin ester as well. The yellow ethereal solution is left to evaporate spontaneously, and, when no more ether can be detected, is placed in a desiccator for twelve hours. After

weighing, the residue is returned to the desiccator for a further twelve hours and is then re-weighed, the mean of the two results being taken as the normal.

(*f*) *Resin estimation*—

To determine the resin ester, the brown alkaline resin solution separated from the ethereal liquid is precipitated with dilute hydrochloric acid, filtered through a tared filter, and washed, by means of the aspirator, in a minimum of water until the washings cease to give a reaction for chlorine. The resin, dried at 80° C. until constant, is then calculated in percentages. In addition, the ratio between the resin ester and cinnamëin must be calculated.

(*g*) *Sp. gr. determination*—

By these means the author obtained results varying between the following extreme values from various commercial balsams—

| | |
|---|---|
| Sp. gr. | 1·135–1·145 |
| Acid value (direct) | 60·0– 80·0 |
| Ester value | 180·0–200·0 |
| Saponification value (cold) | 240·0–270·0 |
| Resin ester | 20·0– 28·0% |
| Aromatic bodies (cinnamëin, etc.) | 65·0– 77·0% |
| Portion insoluble in ether | 1·5– 4·5% |

In the case of authentically pure, natural Honduras balsam the values given below were found—

| | I. | II. | III. |
|---|---|---|---|
| Acid value (direct) | 77·46 | 76·92 | 77·34 |
| Ester value | 165·61 | 137·42 | 137·67 |
| Saponification value (cold) | 243·07 | 214·34 | 215·01 |
| Aromatic bodies (cinnamëin, etc.) | 71·41% | 77·56% | 73·63% |
| Resin ester | 15·70% | 13·18% | 17·32% |
| Portion insoluble in ether | 4·38% | 4·31% | 3·57% |

The results of the author's researches on Peruvian balsam may be summarised in the following sentences :—

1. Saponification with alcoholic alkali under a reflux condenser ; as also by the aqueous method, wherein steam is blown into the alkaline liquid ; and by the hot method with benzine and alcoholic alkali, under a reflux condenser,—furnishes in all these cases results that are below the truth.

2. Saponification with benzine and alcoholic alkali by the cold process, and titration after dilution, gives a more sharply defined end reaction, and higher, more constant values ; the figures found in the case of the balsams examined being 260–270, against 218–259 as formerly given.

3. In determining the acid value direct, extreme dilution is necessary. The balsams examined gave values 68–80, agreeing with older figures.

4. Adulterants increase the acid value and reduce the cold saponification value, so that these changes indicate adulteration.

5. The ester value determined by difference varied only between 188 and 196 in the samples tested by the author, whereas earlier workers record 155–206.

6. An unduly low ester value indicates adulteration, and if it fall below 100 the presence of colophony, Tolu balsam, or benzoin may be inferred.

7. The estimation of the portion insoluble in ether is useful as a means of identification, but not in detecting adulteration. The proportion of this insoluble matter varied from 1·5 to 3 per cent. in the commercial varieties tested.

8. The percentage of cinnamëin in the specimens examined ranged from 65 to 75 per cent., and the resin ester from 20 to 28 per cent., the ratio being 1 : 3 on the average. Ratios of 1 : 2 and 1 : 5 indicate considerable adulteration. In point of value, a balsam rich in cinnamëin is superior to one rich in resin ester.

9. The refractive index of Peruvian balsam lies within the figures 1·42 and 1·49, corresponding to the 100° scale of the butter refractometer.

10. The critical temperature of Peruvian balsam is indeterminable, and the Maumené value is useful merely as a means of identification.

The author has also applied this method to a number of adulterated samples, with the results given in the subjoined Table :—

I. Acid value (direct)—

| Peruvian balsam adulterated with— | 5% | 10% | 20% |
|---|---|---|---|
| Copaiba balsam | 68·04 | 72·24 | 84·2 |
| Storax | 91·00 | 76·16 | 84·28 |
| Colophony | 91·00 | 148·96 | 166·32 |
| Benzoin | 92·40 | 116·20 | 167·44 |
| Castor oil | 113·12 | 118·72 | 130·48 |
| Tolu balsam | 140·00 | 148·96 | 166·32 |
| Turpentine | 66·64 | 62·60 | — |

II. Saponification value (cold)—

| Peruvian balsam adulterated with— | 5% | 10% | 20% |
|---|---|---|---|
| Copaiba balsam | 246·0 | 240·0 | 212·8 |
| Storax | 254·0 | 249·0 | 240·0 |
| Colophony | 252·0 | 252·0 | — |
| Benzoin | 240·8 | 236·6 | 232·0 |
| Castor oil | 243·6 | 236·6 | 229·6 |
| Tolu balsam | 258·0 | 252·0 | 243·0 |
| Turpentine | 252·0 | 235·0 | 212·8 |

III. Ester value—

| Peruvian balsam adulterated with— | 5% | 10% | 20% |
|---|---|---|---|
| Copaiba balsam | 178·96 | 167·76 | 137·41 |
| Storax | 183·44 | 172·84 | 155·72 |
| Colophony | 161·00 | 104·04 | 65·68 |
| Benzoin | 148·40 | 120·40 | 61·62 |
| Castor oil | 130·48 | 117·88 | 99·12 |
| Tolu balsam | 118·00 | 103·24 | 77·28 |
| Turpentine | 186·35 | 172·40 | — |

IV. Cinnamëin and aromatic constituents; also resin ester—

| Peruvian balsam adulterated with— | Resin % | Cinnamëin % | Resin % | Cinnamëin % | Resin % | Cinnamëin % |
|---|---|---|---|---|---|---|
| Copaiba balsam | 24·05 | 65·95 | 27·98 | 63·03 | 31·90 | 60·82 |
| Storax | 17·28 | 72·35 | 18·06 | 73·02 | 19·06 | 73·70 |
| Colophony | 17·50 | 73·25 | — | — | — | — |
| Benzoin | 22·90 | 68·05 | 22·56 | 69·25 | 21·56 | 63·40 |
| Castor oil | 21·00 | 73·50 | 20·36 | 74·68 | 16·88 | 80·10 |
| Tolu balsam | 27·32 | 67·05 | 25·72 | 67·76 | 31·44 | 60·07 |
| Turpentine | 25·78 | 65·02 | 26·10 | 62·08 | — | — |
| | 5% | | 10% | | 20% | |

V. Portion insoluble in ether—

| Peruvian balsam adulterated with— | 5% | 10% | 20% |
|---|---|---|---|
| Copaiba balsam | 0·96 | 1·06 | 0·98 |
| Storax | 1·86 | 1·24 | 0·66 |
| Colophony | 1·70 | 1·62 | 1·05 |
| Benzoin | 1·12 | 0·82 | 0·56 |
| Castor oil | 0·54 | 0·92 | 0·52 |
| Tolu balsam | 0·56 | 0·50 | 0·28 |
| Turpentine | 0·94 | 0·92 | 0·61 |

From these data we may conclude that—

1. Adulterants increase the acid value and depress the saponification value; hence low saponification values and high acid values indicate adulteration.

2. An unduly low ester value points to adulteration, one below 100 indicating falsification with colophony, Tolu balsam, or benzoin.

The author agrees with Gehe & Co. that a Peruvian balsam should contain at least 65 per cent. of cinnamëin (K. Dieterich method) and not more than 28 per cent. of resin ester, the value of the balsam being in direct proportion to the amount of cinnamëin, and in inverse ratio to the quantity of resin present. The Honduras balsams contain over 70 per cent. of cinnamëin. In order to avoid laying

too stringent requirements on commercial grades, the author proposes 240 as the minimum saponification value. Both Gehe & Co. and Caesar & Loretz refer to the author's method, and the results obtained therewith, as marking a further advance in the analysis of Peruvian balsam.

Gehe & Co. found—

| | |
|---|---|
| Cinnamëin content . . . . | 57–60 per cent. |
| Saponification value (hot), of the same . | 235–238 ,, |

by the following method :—

About 5 grms. of Peruvian balsam were shaken up with 5 grms. of water and an equal quantity of standard caustic soda solution, the cinnamëin being then extracted by a triple agitation with 10 grms. of ether each time, expelling the solvent in the water bath, and weighing the residual cinnamëin. Some time was required to expel the final traces of ether, and frequent weighings had to be made before the residue attained constant weight. The weighed residue was treated with 35–40 c.c. of alcoholic $\frac{n}{2}$ potash and about 20 c.c. of alcohol, and saponified in the water bath. The excess of alkali was titrated back with $\frac{n}{2}$ hydrochloric acid.

By this method Gehe & Co. examined a large number of commercial samples of Peruvian balsam, and reported twelve months after their first communication that the percentage of cinnamëin in reliably pure balsams varies between 56·5 and 62·2 per cent., the saponification value (hot) of the cinnamëin being 236–240.

The method of determining the " cinnamëin " laid down in the British Pharmacopœia is as follows :—5 grms. of the balsam is shaken with 5 c.c. of caustic soda solution, sp. gr. 1·16, and then treated three times in succession with 15 c.c. of purified ether. The ethereal solution is collected in a

flask and the ether evaporated off, the residue being dried at a gentle heat until it loses no more than 1 centigramme between two successive weighings; it should then weigh between 2·85 and 3 grms. To the residue 20 c.c. of normal alcoholic potash solution is added, together with 40 c.c. of alcohol, and the saponification is carried on for 1 hour under a reflux condenser, after which the excess of alkali is determined by titration with normal alcohol. The amount of potash thus combined should amount to 11·9 to 12·8 c.c.

Whereas the author, dreading an excessive and too ready volatilisation of the cinnamëin during the evaporation of the solution, therefore avoids resorting to heat for this operation. Gehe & Co. had a different experience, and warmed the solution in an Erlenmeyer flask. The resulting values are consequently somewhat lower than those from the author's method, though the values in each case are concordant.

Finally, mention may be made of the combined method elaborated by Thoms from those of the author and Gehe & Co., because Thoms, as already stated, employed perfectly pure San Salvador balsams obtained direct from the gatherer.

The figures obtained by Thoms are as follows :—

| | | |
|---|---|---|
| Sp. gr. . . . . | 1·139 | |
| Acid value (direct) . . | 83 | (Dieterich method). |
| Saponification value (cold) . | 264 | |
| Insoluble in ether . . | 3·36 per cent. | |

Cinnamëin.—(*a*) By the K. Dieterich method—with this modification, that the ethereal solution of cinnamëin was shaken up twice with 2 per cent. caustic soda, followed by shaking up twice with water, and warming the residue half

an hour in the water bath after the evaporation of the ether—

1. = 60·84 per cent.
2. = 60·88 „
3. = 61·30 „

(*b*) By Gehe & Co.'s method—

4. = 60·52 per cent.
5. = 61·036 „
6. = 60·22 „
7. = 60·768 „

The estimations Nos. 1 and 2 were made by Lüders, No. 3 by Thoms, Nos. 4 to 7 by E. Kennert. Four of the tests were performed by the Gehe method, in order to ascertain the effect of varying durations of the evaporative process on the yield of cinnamëin. The foregoing figures show that no great fluctuations were produced.

Ester value of cinnamëin (Gehe's so-called " saponification value ")—

(*a*) Of the cinnamëin obtained by the Dieterich method—
No. 3. = 239·8
(*b*) Of the cinnamëin from the Gehe method—
No. 7. = 240·9

Resin ester (Dieterich method)—

No. 1. = 20·28
No. 2. = 19·76

Thoms prefers the author's agitation method, but repeated the shaking up several times, and thereby obtained values agreeing with those of Gehe & Co.

The saponification value (hot), or more properly the ester value, of cinnamëin, was determined by Thoms in the following manner :—

The cinnamëin is washed by a little alcohol into a flask, where it is treated for an hour with 50 c.c. of alcoholic $\frac{n}{10}$ potash, and afterwards warmed in the water bath for another hour.

The precipitated potassium salt is redissolved in a little water and, when cooled, the whole is titrated back with $\frac{n}{10}$ hydrochloric acid in presence of phenolphthalein. The difference between this value and 50, multiplied by 0·005616, gives the quantity of KHO consumed in saponifying the cinnamëin present.

The following results were obtained by Hampe in applying the author's method to an adulterated sample of Peruvian balsam :—

| | |
|---|---|
| Acid value (direct) . . . . | 72·90– 74·09 |
| Ester value . . . . . | 145·01–145·04 (!) |
| Saponification value (cold) . . . | 218·3 –219·1 (!) |
| Insoluble in ether . . . . | 0·93 per cent.(!) |
| Cinnamëin and aromatic constituents . | 58·69 ,, (!) |
| Resin ester . . . . . | 24·28 ,, (!) |

The sample did not form a perfectly clear solution in 60 per cent. chloral hydrate. It was very thin, and rather pale in colour, reddish in thin layers.

Since the values given by normal balsam lie within other limits, the saponification value being not less than 140, the insoluble in ether not below 1·5 per cent., and the cinnamein content not lower than 65 per cent., the foregoing balsam was undoubtedly adulterated.

The author found in his researches on Peruvian balsam (*H. A.*, 1896) that adulterants raise the acid and lower the saponification values. Perfectly pure balsams contain up to 4 per cent. of matters insoluble in ether, and form a perfectly clear and complete solution in the aforesaid chloral

hydrate solvent. From these results, it is evident that the author's method answers well in practice.

The following methoxyl values were obtained by Gregor :—

1. 16·7
2. 21·8
3. 22·6

With regard to the German Pharmacopœia tests for Peruvian balsam, the reader is referred to the author's paper in the *Ph. C.*, 1898, No. 19.

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## 13. Tolu Balsam.

*Balsamum de Tolu* (officinal in German Pharmacopœia III.).

**Origin and Habitat.**—*Myroxylon Toluifera* (Papilionaceæ). Northern portion of South America.

**Chemical Constituents.**—Benzoic and cinnamic acids (Devill & Scharling, Flückiger), oily constituents mainly composed of the benzyl ester of benzoic acid, and to a smaller extent of the benzyl ester of cinnamic acid, 7·5 per cent., and toluene ($C_{10}H_{16}$, B.P. 170°) 1 per cent.; impurities, 3 per cent.; vanillin, 0·05 per cent.; cinnamic and benzoic acids, 12–15 per cent.; the toluresinotannol esters of cinammic and benzoic acids (Tschirch). According to Tschirch and Oberländer, the isolated toluresinotannol has the formula $C_{16}H_{14}O_3OCH_3OH$. Trommsdorf found: resin 88 per cent., acids 12 per cent., volatile oil 0·2 per cent.

**General Properties and Commercial Varieties.**—When fresh, the balsam is brownish yellow, quite transparent in thin layers, and free from crystals. Older specimens are hardened, and exhibit a crystalline structure under the microscope; the colour is reddish or yellowish brown; M.P. 60°–65° C.; odour very fragrant, flavour aromatic, sweetish and somewhat pungent. It is soluble in alcohol, chloroform, and alkalis, the alcoholic solution having an acid reaction. The opinion that carbon di-sulphide does not dissolve this balsam (see Detection of Colophony) is untenable, samples being known which give up considerable amounts to this solvent.

**Adulterant.**—Colophony.

**Analysis.**—Earlier examinations of Tolu balsam showed that this product is largely adulterated, mostly with colophony. The practice had been largely promoted by the remarkable requirements laid down by the German Pharmacopœia (D. A. III.), which prescribes "hardened" balsam. The values obtained must therefore be accepted with a certain amount of reserve. The qualitative detection of colophony has been dealt with by Braithwaite, Gehe & Co., Cripps, and Hirschsohn, whilst Thoms and Gehe & Co.

have criticised the German Pharmacopœia tests. Particulars of the Storch-Morawski method for detecting colophony will be found in the description, etc., of that resin. Another point recommended as a special criterion of Tolu balsam, was the degree of solubility in benzol (maximum, 5 per cent.). Quantitative researches, dealing particularly with the determination of the acid, ester, and saponification values, by the usual methods, were first published by Kremel, and afterwards by Beckurts and Brüche.

A. Kremel found—

| | I. | II. |
|---|---|---|
| Acid value (direct) | 127·2 | 100·6 |
| Ester value | 26·7 | 58·7 |
| Saponification value (hot) | 153·9 | 159·3 |

Beckurts and Brüche obtained the following results :—

| | |
|---|---|
| Sp. gr. | 1·092–1·101 |
| Acid value (direct) | 106–132 |
| Ester value | 55– 71 |
| Saponification value (hot) | 177–188 |
| Ash | 0·25–1·2 % |

They preferred the Schmidt test to the acid value determination as a means of detecting colophony, since the acid value does not become appreciably high until the proportion of colophony attains 20 per cent. In the Schmidt test, 0·5 grm. of balsam is left in contact with 25 c.c. of carbon di-sulphide for half an hour, with occasional shaking; then filtered, and the filtrate evaporated in a porcelain basin. Colophony, when present, is revealed in the residue by its smell and the green coloration produced on adding a few drops of sulphuric acid to the dissolved residue, also by the Storch-Morawski test. Pure Tolu balsam should be practically insoluble in carbon di-sulphide. According to Braithwaite, however, this solvent removes

cinnamic acid; and this authority prescribed the following modification of the above test :—When 5 parts of the balsam are warmed twice with 25 or 10 parts of carbon di-sulphide, the filtrate should leave, on evaporation, a crystalline residue, which should give a (hot) saponification value of not less than 300 parts KHO per 1000 parts.

Schmidt's results conflicted greatly with those of E. Dieterich (see below), who found nearly 90 per cent. soluble in carbon di-sulphide; and, in any event, this portion of the Schmidt test is uncertain.

E. Dieterich's results are as follows—

| | |
|---|---|
| Acid value (direct) . . . . | 114·80–158·60 |
| Ester value . . . . . | 31·20– 40·50 |
| Saponification value (hot) . . . | 155·30–187·40 |

Solubility in—

| | |
|---|---|
| Alcohol (90 per cent.) } Acetic ether } | complete. |
| Chloroform—almost complete. | |
| Ether . . . | 53·20–87·90% soluble. |
| Benzol . . . | 82·27% to almost complete. |
| Petroleum ether . . | 2·22–10·22% } |
| Oil of turpentine . . | 27·82–54·55% } soluble. |
| Carbon di-sulphide . | 19·60–88·18% } |

These very high rates of solubility in carbon di-sulphide show the unreliability of this portion of the Schmidt test, although it may be presumed that adulterated samples were employed. At any rate, the acid, ester, and saponification values afford a better criterion. Pure Tolu balsam appears to be practically unknown in commerce, a circumstance explaining the small reliance to be placed on the above test. A renewed thorough investigation of this product is urgently required.

The following may be taken as the usual constants for Tolu balsam :—

| | |
|---|---|
| Free acid calculated as benzoic | 7·2–9·8 per cent. |
| Combined acid „ „ | 22·7–36·3 „ |
| Acid value | 112–124·4 „ |
| Ester value | 68·6–88·9 „ |
| Saponification value | 182·8–205·1 „ |
| Iodine value | 62·2–77·8 „ |
| Refractive index at 60° | 1·593–1·595 „ |
| Carbon bi-sulphide extract | 12·4–16·4 „ |
| Saponification value of ditto | 247·4–301·8 „ |

The minimum saponification value of the carbon bi-sulphide extract for Tolu balsam has been stated to be 290.

The figures obtained by Evans for commercial samples may be usefully compared with the above.

| | |
|---|---|
| Free acid calculated as benzoic | 7·1–16·3 per cent. |
| Combined acid „ „ | 19·36–37·7 „ |
| Acid value | 111·3–126 „ |
| Ester value | 70·0–88·1 „ |
| Saponification value | 188·6–204·3 „ |
| Iodine value | 44·1–71·8 „ |
| Refractive index at 60° | 1·593–1·595 „ |

With regard to the testing and solubility of Tolu balsam, Gehe & Co. express themselves as follows—

Under prolonged storage, or as the result of a brief warming in the water bath, the balsam loses 8–10 per cent. in weight, and passes into a brittle condition. The preference given in the Pharmacopœia to hardened balsam, for which tenable grounds are lacking, is the reason why the hard balsams now current in the German drug market are almost exclusively hardened with colophony, which cannot be detected by the test prescribed in the Pharmacopœia. Even pure balsam is not insoluble in carbon di-sulphide, but gives up as much as 25 per cent. to that

solvent. Others even state that some kinds are soluble up to 80 per cent., though the purity of such samples appears to us questionable.

The foregoing opinion agrees with the author's views on the tests and prescriptions of the German Pharmacopœia, and on the carbon di-sulphide test.

The values obtained by the author coincide fairly with those recorded by Beckurts and Brüche, Kremel, and E. Dieterich, and therefore do not need to be cited here. Tolu balsam should contain as little ash as possible.

The methoxyl value is given by Gregor as 41·6–41·7, and by Bamberger as 46·8.

The German Pharmacopœia test for Tolu balsam was discussed by the author in the *Ph. C.*, 1898, No. 19.

A spurious kind of Tolu balsam, which at one time was to be found on the London market, has been reported upon by J. C. Braithwaite (Pharm. J., 58, 307). This was softer and more viscous than the genuine article, and only very few crystals were to be seen under the microscope, whereas with genuine samples they are abundant. The figures for this balsam are, compared with those of a pure sample, as follows :—

| | Genuine. | Spurious. |
|---|---|---|
| Cinnamic acid (M.P. 133°) . . . . | 4·2 % | 1·15 % |
| Soluble in carbon bi-sulphide. . . . | White crystalline | 61·4 % Brown, transparent, viscous |
| Saponification number of soluble portion . | Over 300 | 274 |

It is regarded as probable that this balsam is derived from a species of *Myroxylon* allied to *M. toluifera*.

R. W. Mattison has described a fictitious Tolu balsam containing 63 per cent. of storax.

**Quino-quino Balsam.**—According to C. Hartwich and A. Jama, Tolu balsam, Peru balsam, and Quino-quino balsam are all derived from varieties of the same tree : Tolu balsam

from *Myroxylon balsamum* (L.), var. *A. genuinum* (Baill.), Peru balsam from *M. perierœ* (Baill.), and Quino-quino balsam from *M. balsamum*, var. *J. punctatum* (Baill.). Quino-quino balsam consists of reddish-brown irregular pieces, having a pleasant odour when gently heated, similar to Tolu balsam, and after melting and cooling, exhibiting many crystals under the microscope. The three balsams are compared in the following Table :—

| | Tolu Balsam. | Peru Balsam. | Quino-quino Balsam. |
|---|---|---|---|
| Acid value | 114–158 | 68–80 | 8·03 |
| Saponification value | 155–187 | Ov r 245 | 134·09 |
| Ester value | Up to 73 | At least 165 | 53·79 |
| Cinnamëin | 7·5 % | 62–64 % | 5·83 % |
| Resin | 80 % | 30 % | 78·5 % |
| Vanillin | 0·05 % | 0·046–·05 % | 0·044 % |
| Benzyl benzoate in cinnamëin | Present in quantity | Almost wholly | Almost entirely |
| Benzyl cinnamate ,, | In small proportion | In very small quantity | Traces only |
| Free benzoic acid | Small proportion | None | Almost all |
| Free cinnamic acid | Principally | Exclusively | Minute amount |
| Free resin alcohol | None | None | At least 5·7 % |
| Resinotannol | Tolu-resinotannol ($C_{17}H_{18}O_5$) | Peru-resinotannol ($C_{18}H_{20}O_5$) | Tolu-resinotannol ($C_{17}H_{18}O_5$) |
| Benzoic acid in resin | Small amount | Very small amount | All |
| Cinnamic acid in resin | Principally | Principally | None |

**Cabureiba Balsam.**—A. Tschirch and J. O. Werdmüller have examined a very rare balsam from Brazil which they regard as probably identical with Piso's Cabureiba balsam and Guibort's "baume de Perou brun" or "rouge en coques." This was found to contain free benzoic acid but no cinnamic acid, vanillin and the benzoic ester of cabureibaresinotannol, the resinotannol having the formula $C_{14}H_{18}O_4$. The balsam did not contain any "cinnamëin."

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## CHAPTER II

### RESINS

Before dealing with the resins separately, it may be premised that for this group of substances, just as with the gum resins, much more divergent methods have been employed for determining their characteristic constants than is the case with the balsams. Extracts have been used to some extent which no longer corresponded to the natural drugs; this is sufficient to partly explain the great fluctuations observable in the results, though these are also in some degree attributable to the very dark solutions given by the (mostly coloured) resins.

A series of uniform methods, based on the modern conceptions of the chemistry of resins, tested in practice, and capable of obviating similar inconveniences, was recently made public by the author; it is highly desirable that contributions to the establishment of a uniform system of testing, on a modern basis, should be presented by other workers, or that existing data should be subjected to investigation, in order to furnish the highly necessary accumulation of numerical data.

### 14. Acaroid Resin.

*Resina Acaroïdes* (*Xanthorrhœa Resin*)

I. Red Acaroid Resin (Yacca Gum, Grass Tree Gum)

**Origin and Habitat.** — *Xanthorrhœa Australis*, *X. quadrangularis*, *X. Drummondii*, *X. Preisii*, etc., chiefly

different species of *Xanthorrhœa* (Asphodeleæ). New South Wales.

**Chemical Constituents.**—Paracumaric acid, $C_9H_8O_3$, in a free state 1 per cent.; benzoic acid (traces) and paracumaric acid 2 per cent., both in combination with erythroresinotannol, $C_{40}H_{39}O_9OH$; paraoxybenzaldehyde 0·6 per cent. The bulk, 85 per cent., of the resin consists of the erythroresinotannol ester of paracumaric acid. According to Hildebrand, the absence of cinnamic acid distinguishes this resin from yellow acaroid.

## II. Yellow Acaroid Resin

**Origin and Habitat.**—*Xanthorrhœa hastilis* (Asphodeleæ). Tasmania.

**Chemical Constituents.** — Free paracumaric acid ($C_9H_8O_3$), 4 per cent.; free cinnamic acid, 0·5 per cent.; combined paracumaric acid, 7 per cent.; combined cinnamic acid, 0·6 per cent. Both acids form esters with xanthoresinotannol ($C_{43}H_{45}O_9OH$), producing chiefly the corresponding ester of paracumaric acid, which forms the main constituent of this resin. In addition, there are also probably present styracin ($C_{18}H_{16}O_2$), cinnamic phenylpropyl ester, para-oxybenzaldehyde, and vanillin, the latter, however, being somewhat uncertain (Hildebrand).

**General Properties and Commercial Varieties.**—The *red resin*, or "grass tree gum," forms small, red-brown, dusty lumps, with lustrous fracture, and about 10 per cent. of impurities; it is completely soluble in alcohol, and gives no reaction for cinnamic acid.

The *yellow resin* (Resina lutea, Botany Bay gum) is of a transparent yellow colour, also dusty, and gives the cinnamic acid reaction.

Australian acaroid resins are now being collected, and

are justly recommended as substitutes for colophony, particularly for sizing paper, for which purpose they have long been used in North America, as well as for enriching gas, and in the manufacture of varnishes and perfumery ware. The resins of the various *Xanthorrhœa* species differ not inconsiderably both externally and inwardly (K. Dieterich, *H. A.*, 1897, pp. 37, 38).

**Adulterants, etc.**—Owing to the relatively low price of these resins, the only impurities likely to occur are extraneous mineral and vegetable matters. The different qualities of acaroid resin are also liable to be mistaken one for another.

**Analysis.**—Although actual analytical reports on the acaroid resins are scarce, this technically important material has been mentioned here on account of its introduction into Europe, and employment in the preparation of varnishes, paper, and perfumery. Its application to the production of gas is worthy of mention; and in America it is used medicinally as a tincture (60 grms. of resin per litre of alcohol) in doses up to 70 grms. for phthisis and chronic catarrh. At the present time, acaroid resin from *X. quadrangularis* is obtainable at a low price from Australia, and has rightly found favour.

According to Maiden, the yellow acaroid resin does not soften in the mouth. Petroleum ether dissolves 1–2 per cent., and alcohol, 91–94 per cent. According to the author's researches, the acaroid resin from *X. quadrangularis*, and other red varieties, resembles the yellow resin in containing no cinnamic acid.

The red resin from *X. arborea* is soluble to the extent of about 3 per cent. in petroleum ether, but dissolves entirely in alcohol, except for the 5–10 per cent. of contained impurities. Hirschsohn found three different kinds to be completely

soluble in alcohol, but only imperfectly so in chloroform and ether.

## Acaroid Resin.

**Analysis.**—M. Bamberger found—

I. *Yellow Acaroid*—

| | I. | II. | |
|---|---|---|---|
| Acid value (direct) | 132 | 133 | From purified resin. |
| Saponification value (hot) | 220 | 225 | |
| Methoxyl value | 27·66 | 28·97 | crude resin. |
| Methoxyl value | 34·73 | — | purified resin. |

II. *Red Acaroid*—

| | I. | II. | From |
|---|---|---|---|
| Methoxyl value | 60·3 | 60·9 | crude resin. |
| Methoxyl value | 71·2 | — | purified resin. |
| Carbonyl value | 0·97 | — | purified resin. |

Owing to the dark colour of the red resin solution, the acid and saponification values could not be determined.

The following are analyses of acaroid resins by A. Rud ing :—

| | Water. | Substance Insoluble in Alchol. | Acid Value. | Saponification Value. | Iodine Value. |
|---|---|---|---|---|---|
| Yellow acaroid resin | 5·65 | 0·93 | 82·3 | 98·0 | 176·2 |
| Yellow acaroid resin (Adelaide) | 4·50 | 3·52 | 67·2 | 105·5 | 176·2 |
| Yellow acaroid resin (Victoria) | 4·40 | 0·88 | 72·8 | 164·0 | 175·0 |
| Red acaroid resin | 4·90 | 5·26 | 18·5 | 67·7 | 164·5 |

Schimmel & Co. report the following values for yellow acaroid resin oil :—Acid value (direct), 4·9; ester value 69·4; and saponification value (hot), 74·3. This oil is practically unimportant.

Kitt found the following carbonyl values :—

| | |
|---|---|
| Yellow acaroid resin | 0·29–0·46 |
| Red do. | 0·84 0·98 |

On the worth of these values, the author expressed himself in *Chem. Rev.*, 1898, No. 10 (see also Wiesner, *Die technisch verwendeten Gummiarten, Balsame, und Harze*, pp. 189–195). In view of the important technical future before the acaroid resins, further analytical data are highly desirable.

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## 15. Amber.[1]

*Succinum, Succinite*

**Origin and Habitat.**—*Pinites succifer* (primeval) (Abietineæ). Prussian Baltic coast.

**Chemical Constituents.**—The borneol ester of succinoabietic acid, 30 per cent.; free succinoabietic acid ($C_{80}H_{120}O_5$), 28 per cent.; succinic succinoresinol ester ($C_{12}H_{20}O$), 70 per cent. When hydrolysed by alcoholic caustic potash, succinoabietic acid yields a divalent alcohol—succinoabietol ($C_{40}H_{60}O_2$) and succinosilvic acid ($C_{24}H_{36}O_2$). Succinic succinoresinol ester is an oxidation product of succinoabietic acid. The portion of succinite insoluble in alcohol consists entirely of the succinic ester of succinoresinol, which contains 0·47 per cent. of sulphur. According to Aweng succinite contains sulphur.

*Gedanite* has the same constituents as succinite, except that sulphur is absent. Owing to its inferior hardness as

[1] The collective term "amber," which comprises a number of fossil resins, such as Succinite, Glessite, Stantienite, Beckerite, etc., is restricted here to Succinite, or true amber.

compared with succinite, Helm termed this variety "friable amber." *Glessite* appears to agree with succinite in composition, except that, instead of borneol, it contains a substance recalling carvol. *Allingite* contains sulphur, but neither borneol nor succinic acid; and, according to Aweng, the resin acid it yields is not identical with succinic acid.

**General Properties and Commercial Varieties.**—*Succinite*: yellow or yellowish brown, translucent or opaque, brittle lumps, with lustrous conchoid fracture; melting-point, 250°–300° C., sp. gr. 1·07–1·08.

*Gedanite* is of whitish yellow colour and transparent, without fluorescence or polarisation; readily fractured; froths up at 140° to 180° C.

*Glessite* when examined under the microscope (100 diameters) exhibits a cellular, globular structure, with granular contents. It has the same melting-point as succinite.

*Allingite* is whitish yellow to reddish in colour, melts at 300° C., and is of sp. gr. 1·076.

*Amber-guaiacum resin* is not an amber, but a good quality of guaiacum (*q.v.*). The amber from the Baltic coast is specially known as Baltic amber.

The so-called "pressed amber," or "ambroid," is prepared in plates, by placing small assorted pieces of amber in cast-steel moulds at a temperature of 200°–250° C., and exposing them to a pressure of about 400 atmos.

The waste pieces, from $\frac{1}{24}$ to $\frac{1}{4}$ inch diameter, are used up for making varnish, amber resin, and succinic acid.

**Adulterants, etc.**—Copal, colophony, and artificial amber.

**Analysis.**—The present is not a suitable occasion for discussing closely the many valuable contributions made

by O. Helm,[1] or for reporting all the properties of the various kinds of amber mentioned above. A few important data that may be useful to the analyst in the differentiation of the various grades are, however, quoted from the publications of Helm and Potonié.[2] According to the latter, the following varieties of amber should be regarded as distinct :—

I. *Gedanite :* pure yellow, transparent, frothing up at 140°–180° C. and melting when heated further; also called "friable amber"; this variety contains less succinic acid than succinite.

II. *Glessite :* usually brown and opaque.

III. *Stantienite,* or "black resin" : very brittle and pulverulent.

IV. *Beckerite,* or "brown resin" : opaque and viscous.

V. *Succinite,* or "true amber" : sp. gr. 1·050–1·096, —M.P. 250°–300° C.

(For a description of Silician and Roumanian amber, see O. Helm, *A. d. Ph.* 218, pp. 307, 447.)

In working up amber into varnish, it is melted or distilled (compare copal and dammar), the amber oil being then used as a solvent. When melted or distilled, amber is more readily soluble in oil of turpentine and fatty oils than in the crude state.

It should be stated that amber is liable to be confounded with copal, which is employed to adulterate it, and that they may be differentiated by the fact that amber is insoluble in cajuput oil, which completely dissolves copal (*q. v.*).

With regard to the detection of amber substitutes, J. Marcusson and G. Winterfeld remark that copal, and especially hard Zanzibar copal, of all substances most

[1] Particularly *A. d. Ph.* 213, 215, and 222.
[2] *Ph. C.*, 1890, p. 744.

nearly resembles amber. Copal can, however, be distinguished from amber by the absence of succinic acid in the distillate, also by its greater solubility in cajuput oil. The hardened copal prepared by the method of Spiller (Ger. Pat. 207,744 of 1907) may, however, contain succinic acid, and, moreover, it is insoluble in cajuput oil. The latter can be identified by its low ester value (*i. e.* 8·2–9·4, whereas that of amber is 71–112), and also by its high acid value (*i. e.* 56·2–71·4), that of amber being only 15–35. The sulphur content of the resin, however, offers a very simple means of distinguishing between the two, the amount of sulphur in amber varying from 0·34 to 0·42 per cent., while in three samples of the artificially hardened copal it was found to be 0·06, 0·04, and 1·0 per cent. respectively. These authors prefer to use a mixture of equal parts of benzene and alcohol in place of absolute alcohol, as they find it a better solvent in the estimation of the acid and ester values.

In order to distinguish amber from copal, F. Klein proposes the following test :—A small portion of the powdered sample is mixed with about 4 c.c. of ethyl acetate containing about half a grm. of cobalt nitrate, 2 c.c. of anhydrous acetic acid and 1 or 2 c.c. of chloroform are also added and the mixture is heated. Copal dissolves entirely in this mixture, whereas amber only granulates but does not dissolve. On mixing the liquid with strong methyl alcohol a precipitate is formed having a silky lustre.

According to Flemming, both copal and amber are soluble in the chlorhydrins of glycerin (epi-dichlorhydrin)—see Table, pp. 30–32; and true copal (not copal from *Dipterocarpeæ* and *Coniferæ !*—see Copal) is practically insoluble in 60 per cent. chloral hydrate. Furthermore, copal gives no ester value, whereas amber does; in addition, copal is characterised by its ready solubility in ether and

cajuput oil, as well as by the negative results furnished by testing a burning sample with paper moistened with lead acetate (absence of volatile sulphur compounds which escape from heated amber as secondary compounds and stain the test paper black). Amber is artificially imitated by coloured glass, celluloid, or colophony with artificial adjuncts. To detect colophony it is merely necessary to drop a little alcohol or ethylsulphuric acid on the suspected sample; pure amber is unattacked by these reagents, whereas an impure specimen will show a dull spot. The melting point also affords a definite indication of purity. Celluloid may be distinguished by its softness and by the odour of camphor which it evolves on heating or when it is rubbed.

Since it may happen that a large block of amber has been artificially prepared by pressing together a number of small fragments of amber, so that, by this means, inferior waste is worked up into apparently valuable large pieces, O. Helm devised a method for detecting such artificial products. With regard to " imitation amber " he says—

" When polished, the transparent pressed blocks exhibit a peculiarity distinguishable by none but a skilled eye, namely, when the block is held up to the light, so far from its structure being perfectly homogeneous, the whole interior seems to be traversed by a number of hazy wave-like films, which are in reality the surfaces of contact of the individual lumps composing the block.

" Under polarised light this pressed amber behaves in a very characteristic manner. When placed between crossed Nicol prisms, polished Baltic amber reveals faint, but seldom bright, interference bands. On rotating the polariscope through 90° the colours pass into their complementaries, and return to their original condition when the rotation attains 180°, thus changing twice during a complete revolution.

The usual colours observed are red, green, and orange, to blue. A block composed of small fragments of amber pressed together always exhibits bright interference bands, both adjacent and frequently intermixed, which vary according to the size of the constituent fragments, on changing the field of vision. Frequently all shades of colour can be seen in the field at once, which change into their complementaries on the polariscope being rotated through 90°."

In the less transparent kinds of amber this means of differentiation is not so readily applicable. Klebs, however, discovered another characteristic indication. As already observed by Helm, in 1878, all cloudy and opaque kinds of amber, when viewed under the microscope, exhibit in their interior a number of round, oval, or elongated cavities of various dimensions. The size, position, and number of these cavities differ greatly, giving rise to the different qualities of commercial clouded amber. Under the heavy pressure (up to 3000 atmos.) employed in making the artificial blocks, these cavities are compressed, and, when viewed under the microscope, exhibit a flattened, often dendritic appearance. In addition, it is stated by Klebs that clouded pressed amber can be recognised by the more cloudy appearance of the clear matrix, the turbid portions being seemingly arranged in parallel strips, like cirrhus clouds. At the planes of transition between the clear and clouded parts, the yellowish red tinge produced by transmitted light and the bluish sheen by reflected light (with dark background) are thrown up more distinctly by the extremely fine cavities than is the case with natural amber.

O. Rössler reports as follows on the differentiation between copal and amber :—

" To decide whether a sample is true amber or a fossilised

East African copal, the sulphur content should be examined. When a fragment of amber is heated in a small glass tube, fused at the lower end, volatile sulphur compounds are evolved, which will blacken a piece of paper, moistened with lead acetate, held at the open end of the tube. On the other hand the copals, of whatever origin, are free from sulphur. Samples of amber from Troy and Mycene were found to be true amber."

In addition to the differential characteristics of the various kinds, and the adulterations already mentioned, a number of purely analytical data are available.

Thus Williams found—

| | |
|---|---|
| Acid value (direct) | 15·4 |
| Ester value | 71·4 |
| Saponification value (hot) | 86·8 |
| Iodine value | 62·10 |
| Moisture | 1·05 per cent. |
| Ash | 0·28 „ |

A. Kremel found—

| | I. | II. |
|---|---|---|
| Acid value (direct) | 34·4 | 33·4 |
| Ester value | 74·5 | 91·1 |
| Saponification value (hot) | 108·9 | 124·5 |

The concordance here is not very striking.

Von Schmidt and Erban's results are as follows :—

| | |
|---|---|
| Natural amber—Saponification value (hot) | 144·8 |
| Fused amber—Saponification value (hot) | 36·0 |
| Iodine value | 4·8 |

values which, although determined by the same methods as those used by the earlier investigators, agree but poorly with them. The solubility of amber in a number of solvents is given by von Schmidt and Erban as follows :—

| Solvent. | Fused Amber. | Natural Amber. |
|---|---|---|
| Alcohol | almost insoluble | almost insoluble. |
| Ether | partly soluble | almost insoluble. |
| Methyl alcohol | almost insoluble | almost insoluble. |
| Amyl alcohol | partly soluble | almost insoluble. |
| Benzol | almost entirely soluble | almost insoluble. |
| Petroleum ether | almost insoluble | almost insoluble. |
| Acetone | almost insoluble | insoluble. |
| Glacial acetic acid | partly soluble | almost insoluble. |
| Chloroform | partly soluble | almost insoluble. |
| Carbon di-sulphide | almost entirely soluble | partly soluble. |
| Oil of turpentine | almost entirely soluble | partly soluble. |

Mills and Muter found the saponification value to be 161 and the bromine value 53·5.

As already mentioned, amber, being an esteriferous resin, yields an ester value, and is therefore distinguishable by analytical means from copal, which contains no esters.

C. Coffignier obtained the following results with a specimen of amber :—

| | |
|---|---|
| Specific gravity | 1·052 |
| Melting point | 300° |
| Acid value | 97 |
| Saponification value | 115 |

The solubility of the amber in various solvents are as under :—

| | |
|---|---|
| Ethyl alcohol | 14·3 per cent. |
| Methyl alcohol | 11·3 „ |
| Amyl alcohol | 24·2 „ |
| Ether | 18·8 „ |
| Chloroform | 17·3 „ |
| Benzene | 21·2 „ |
| Acetone | 23·3 „ |
| Turpentine | 16·9 „ |
| Benzaldehyde | 32·1 „ |
| Aniline | 30·7 „ |
| Amyl acetate | 30·0 „ |
| Carbon tetrachloride | 11·5 „ |

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## 16. Anime.

*Resina Anime.*

**Origin and Habitat.**—The source of this resin is very uncertain, there being a number of other closely allied kinds, such as elemi, Resina kikekunemalo, Resina tacamahaca (*q. v.*). In England the name "anime" is applied to copal, the soft varieties in particular, and some French drug merchants call Madagascar copal, "animé." The resin from *Hymenæa Courbaril* is an entirely different product to West or East Indian anime, and the reason that anime has been erroneously confounded with Courbaril resin (Schmidt's *Organ. Chemie*, 1896; Kolbe's *Organ. Chemie*, 1868), and *H. Courbaril* regarded as the source of anime, is because Courbaril resin is called "American copal," and, as a soft copal, is termed "anime" in England. Even a superficial examination of anime resin and its odour will be sufficient to clearly show that it has nothing in common with Courbaril and Madagascar copals. Anime is more nearly allied to elemi, whilst Courbaril and Madagascar resins are more nearly allied to true copal. Probably, like elemi, anime is obtained from a species of Icica (Burseraceæ). West and East Indies.

**Chemical Constituents.**—Resin soluble in cold alcohol, 54·30 per cent.; pale yellow gelatinous sub-resin, resembling turpentine in appearance, insoluble in cold,

but soluble in hot, alcohol, 42·80 per cent.; ethereal oil, 24 per cent. (Paoli).

**General Properties and Commercial Varieties.**—*West Indian anime* is in the form of brittle lumps, covered outside with white dust, yellowish white in colour internally, with a slight resinous lustre, smelling more like elemi than incense, and softening like mastic when chewed. It is almost completely soluble in hot alcohol, but only imperfectly so in cold alcohol or benzine. This variety is darker than that from the East Indies.

*East Indian anime* takes the form of masses composed of smaller, rounded, irregular granules, of uneven reddish yellow colour, which are brittle and of waxy, lustrous fracture. It is more difficult to soften than the above variety, and is lighter coloured and stronger smelling—the odour resembling that of dill and fennel.

**Adulterants, etc.**—Vegetable and mineral substances.

**Analysis.**—As no pure or characteristic specimens of this product are at present to be met with in commerce, the practical absence of analytical data is not surprising. Within the last decade anime was still an article of trade, but has now almost entirely disappeared. Williams examined several kinds of the natural product, by the usual methods, and obtained the following values :—

| | I. | II. | III. |
|---|---|---|---|
| Acid value (direct) . . . | 26·6 | 18·2 | 25·2 |
| Ester value . . . . | 47·0 | 55·4 | 62·3 |
| Saponification value (hot) . | 73·6 | 73·6 | 87·5 |
| Iodine value . . . . | — | 135·25 | — |
| Moisture . . . . | 0·1% | 0·48% | 0·31% |
| Ash . . . . . | 0·05% | 0·11% | 0·07% |

Hirschsohn found the following values for the (dried) constituents soluble in petroleum ether at 120° C. :—

| | |
|---|---|
| Anime occidentale . . | 72·89 per cent. soluble. |
| Do. orientale . . . | 74·05 „ „ |
| Do. do. . . . | 65·05 „ „ |
| Do. do. . . . | 77·85 „ „ |

The author has examined East and West Indian anime by the same methods as those used by Williams, and found the values given below :—

| | East Indian. | | West Indian. | |
|---|---|---|---|---|
| | I. | II. | III. | IV. |
| Acid value (direct) . | 29·69 | 30·64 | 45·36 | 47·20 |
| Ester value . . | 29·77 | 38·76 | 113·93 | 102·39 |
| Sapon. value (hot) . | 59·46 | 69·31 | 159·29 | 149·59 |

The figures for I. and II. agree closely with those found by Williams, so that possibly the specimens examined by that worker were also East Indian anime. The values for the West Indian variety are seemingly much higher than those furnished by East Indian anime.

Mills and Muter found for anime :—saponification value 95, and bromine value 60·2.

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## Artificial Resins.

The artificial resins may be divided into two classes, those produced by the esterification of colophony, and the condensation products of formaldehyde and phenols.

The products of the first class are formed by heating colophony with alcohols (*e. g.* glycerin) at a high temperature, either under pressure or in a vacuum. The products are said to resemble the copals and are referred to as " ester "

gums. Owing to their low acid value they are specially suited for the preparation of acid-free lacquers for metallic paints. According to W. Lippert and H. Reissiger these ester gums are never perfectly neutral, samples examined by them having acid values ranging from 17 to 45. The esters can only be saponified with great difficulty. The authors consider that a good " ester " gum should have an acid value not exceeding 20.

The other class of artificial resins are formed by treating a mixture of phenol and formaldehyde with either hydrochloric acid or caustic soda, under suitable conditions, when a condensation product is quickly formed as a solid, hard, pinkish mass.

In this reaction phenol may be replaced by cresols, naphthols, thymol, etc., and in place of formaldehyde any polymer or derivative may be employed, and in certain cases, acetaldehyde, benzaldehyde, etc.

L. V. Redman, A. J. Waith and F. P. Brook regard the reaction as taking place in two stages, in the first of which oxybenzyl alcohol is formed, while in the second two molecules of oxybenzyl alcohol condense with formation of saligeno-saligenin and elimination of water.

(1) $C_6H_5OH + CH_2O = HOCH_2 . C_6H_4OH$
(2) $2HOCH_2 . C_6H_4OH = HOCH_2 . C_6H_4 . OCH_2 . C_6H_4OH + H_2O.$

An account is given of an investigation into the reaction which takes place between hexamethylene-tetramine (formed by the action of ammonia on formaldehyde) and phenol, in which it is shown that when the materials are perfectly dry, ammonia alone is given off, the reaction being strictly quantitative.

One of these synthetic resins known as " Bakelite " is prepared by the process patented by Dr. Bakeland, one of

the chief workers in this line. Below are given the analyses of two of Bakeland's products together with those of the above author's, as well as the calculated figures for the two formulæ to which they closely approximate—

| | Dr. Bakeland's Resins. | | | | Resins prepared by Redman, Waith and Brook. | |
|---|---|---|---|---|---|---|
| | Phenol and Formaldehyde. | | Phenol and Saligenin. | | | |
| Carbon | 77·04 | 77·95 | 78·16 | 78·24 | 77·98 | 77·96 |
| Hydrogen | 5·79 | 5·97 | 5·65 | 5·75 | 6·17 | 6·23 |
| Oxygen | 16·17 | 16·08 | 16·19 | 16·01 | 15·85 | 15·81 |

| | Calculated for | |
|---|---|---|
| | $C_{104}H_{92}O_{16}$. | $C_{90}H_{80}O_{14}$. |
| Carbon | 78·16 | 78·04 |
| Hydrogen | 5·81 | 5·88 |
| Oxygen | 16·03 | 16·16 |

$C_{104}N_{92}O_{16} = 14\ (C_7H_6O)\ .\ C_6H_5O\ .\ H_2O$, or 14 methylenes and 15 phenols. $C_{90}H_{80}O_{14} = 12\ (C_7H_6O)\ .\ C_6H_5O\ .\ H_2O$, or 12 methylenes and 13 phenols.

On heating 10 mols. of phenol with 1 mol. of hexamethylene tetramine until all ammonia is evolved, a heavy viscous liquid is obtained, which becomes semi-solid on cooling, and contains 63 per cent. of phenyl-endeka-saligeno-saligenin; this the writers term "novolak." The latter, again heated with sufficient hexamethylene tetramine to bring the proportions of methylenes and phenols to 1 : 1, yields a porous, spongy mass, which on powdering and heating under a pressure of 12,000 lbs. per sq. in. in moulds at 200° C. for 5 to 10 minutes, yields a transparent product resembling amber, which has a dielectric strength of 50,000 to 90,000 volts per mm.; a resistance of $2 \times 10^9$ ohms per cm. and a tensile strength of 4,000 to 5,000 lbs per sq. in.

The analyses of several of these products gave a mean of—

| | |
|---|---|
| Carbon | 75·4 |
| Hydrogen | 5 9 |
| Oxygen | 18·7 |

which corresponds to the formula 77 $(C_7H_6O)$ 20 $(C_2H_4O_2)$.

The group $C_7H_4O_2$ being regarded as an oxidation product in which two hydrogens have been replaced by one oxygen.

The physical tests show these synthetic resins to be of considerable value. The tensile strength depends upon the temperature and the time of heating, but, speaking generally, it ranges from 1,400 to 4,400 lb. per sq. in., the moulding pressure largely increasing the strength. The crushing strength varies from 7,456 to 32,000 lb. per sq. in. The dielectric strength of discs $\frac{1}{2}$ mm. thick gave voltage puncture tests of 40,000 to 50,000, rubber giving 38,000 and ebonite 30,000, while the specific electrical resistance varied, also according to time of heating and temperature to which the product had been submitted, from $2{\cdot}7 \times 10^6$ to 2,800 $\times 10^6$.

For further particulars see the comprehensive paper by L. V. Redman, A. J. Waith and F. P. Brook (*The Jour. of Ind. and Eng. Chem.*, 1914, p. 3), which gives a very full historical account of the subject; also patents by Dr. Bakeland (*e. g.* Fr. Pat. 386,627, 1908; Eng. Pat. 21,506, 1908), and many others.

### Benzoin, Benzoinum.

A resin obtained from *Styrax benzoin* (Dry.) and also probably from other species. Siam, Sumatra, Borneo, Java, and other East Indian islands.

### 17. Siam Benzoin.

*Resina Benzoës* (officinal in German Pharmacopœia).

**Origin and Habitat.** — *Styrax Benzoin* (Styraceæ), (*S. benzoides*, Kerr). Siam.

**Chemical Constituents.**—Oily neutral liquid, an ester of benzoic acid (the alcohol being probably cinnamic or benzyl alcohol), 0·3 per cent.; vanillin, $C_8H_8O_3$, 0·15 per

cent.; free benzoic acid, 2–4 per cent.; impurities, 1·6–3·3 per cent.; benzoic benzoresinol ester, and benzoic siaresinotannol ester. Benzoresinol has the formula $C_{16}H_{26}O_2$; siaresinotannol, the formula $C_{12}H_{14}O_3$. The bulk of Siam benzoin consists of the mixture of benzoic benzoresinol ester and benzoic siaresinotannol ester:—

| | | |
|---|---|---|
| Benzoic acid . . . . | 38·2 per cent. | |
| Siaresinotannol . . . | 56·7 „ | |
| Benzoresinol . . . . | 5·1 „ | (Lüdy). |

According to Stolze the white tears and the surrounding resin contain the same proportion of benzoic acid, but Kopp did not find this to be the case, since the former yielded 8 to 10 per cent. of acid and the latter 18 per cent. Bucholz found 12·5 per cent., and Stolze 19·8 per cent. of benzoic acid in the resin, but higher results than these are obtained from the saponification value, *i. e.* from 22 to 34 per cent. The resin should be almost entirely soluble in alcohol. Sumatra benzoin, however, contains a higher percentage of insoluble than the others; thus R. C. Pursel and W. Graham found in six samples of benzoin in the United States an average of 86 per cent. of soluble matter, while Barclay found 69·9 per cent. as the average of ten samples on the London market. The matter insoluble in alcohol usually amounts to 4 or 5 per cent. in Siam benzoin and 10 or 15 per cent. in the Sumatra variety.

**General Properties and Commercial Varieties.**—Whilst *Siam benzoin* is in the form of smooth, rounded, brownish lumps, white inside and generally light coloured and pure, the other varieties—such as *Sumatra*, *Padang*, *Penang*, and *Palembang* benzoin—are impure blocks or masses of a reddish-grey or greyish-brown colour, with isolated embedded pale-coloured or white, brittle and soft

tears, and containing pieces of bark and chips of wood. Siam, Padang, and Palembang benzoin contain no cinnamic acid, which, however, is present in the Sumatra and Penang varieties. Fragrant odour but practically no taste except after long chewing. Siam benzoin is the best kind, Palembang and Sumatra coming next in order: sp. gr. 1·063–1·092.

**Adulterants, etc.**—Siam benzoin is adulterated with Padang and Palembang benzoin, and with mechanical impurities; Sumatra benzoin, with Palembang, and mechanical impurities, colophony, dammar, storax, and turpentine.

**Analysis.**—A number of authors, among whom may be mentioned Stolze, Grassmann, Helmstädt, Frémy, v. d. Pliet, Wach, Unverdorben, Kopp, Hirschsohn, etc., have examined the various benzoins, more especially for their solubility, ash content, adulterants, etc. For the most part the distinctive tests applied were merely qualitative; a very comprehensive paper published some years ago in the *A. d. Ph.* (200, p. 205) deserves mention here on account of its valuable character. Subsequently Hirschsohn examined the various kinds as to their percentage content of substances soluble in petroleum ether; and later quantitative determinations were made by Kremel, Schmidt and Erban, Beckurts and Brüche, Helbing, Lüdy, E. Dieterich, Evans', Dunlop, K. Dieterich, and others. Fr. Lüdy, to whom we are indebted for an accurate knowledge of the different kinds of benzoin, and who has examined them on the basis of modern resin chemistry, must be considered as an experienced authority on these products. He states that the very fluctuating values obtained are attributable to the lack of uniform methods. Unfortunately no one but the author appears to have investigated pure and adulterated benzoins on the lines of more recent experience.

According to Lüdy, Siam and Palembang benzoin differ from Sumatra and Penang benzoin by the fact that the former contain benzoic acid and the latter cinnamic acid. It may also be mentioned that the author has reported obtaining the reactions of cinnamic acid with a Siam benzoin from the London market; Siam benzoins containing cinnamic acid would therefore appear to exist, even though rarely met with. Helbing has shown that benzoin which he obtained from the London Docks was largely adulterated with artificial products, containing sand, resin, and talc.

The solubility in petroleum ether was found by Hirschsohn to be—

| | Dried at 17° C. | at 120° C. |
|---|---|---|
| Siam benzoin . . . . | 27·53 | 16·49 |
| Do. . . . . | 26·66 | 21·19 |
| Do. in grains . . | 28·73 | 17·49 |

The acid, ether, saponification, and methoxyl values have also been determined. The figures quoted by Williams cannot be taken into consideration, the variety of benzoin not being specified. For the sake of completeness, mention is made of the colour reactions obtained by Mauch with benzoin and chloral hydrate, without crediting them with more value than colour reactions in general. Von Schmidt and Erban have also reported on the solubility, acid value, and saponification value of benzoin, but without indicating the variety examined. The detection of colophony in benzoin by the Storch-Morawski reaction will be found under "Colophony."

A. Kremel, using an extract of the resin, found—

| | |
|---|---|
| Acid value (direct) . . . . . | 141·1 |
| Ester value . . . . . | 55·4 |
| Saponification value (hot) . . . | 196·5 |

but as the natural drug was not employed these figures have a merely relative value.

Beckurts and Brüche's results are given below—

| | | |
|---|---|---|
| | Sp. gr. | 1·150–1·171 |
| | Ash | 0·27–1·04 per cent. |
| | Insoluble in alcohol | 2·1–4·0 ,, |
| From extract | Acid value (direct) | 119–167 |
| | Ester value | 39– 60 |
| | Saponification value (hot) | 172–211 |

The same remark applies to these last three values as to those of Kremel, and also the following by E. Dieterich :—

| | | |
|---|---|---|
| From an extract | Acid value (direct) | 140·0 |
| | Ester value | 35·0 |
| | Saponification value (hot) | 175·0 |

All the foregoing authors worked with extracts, and by the usual methods.

Evans' found 1·30–2·48 per cent. of matters insoluble in alcohol.

E. J. Parry gives the following figures :—

| | |
|---|---|
| Mineral matter | 0·24–1·98 |
| Soluble in alcohol | 88–96·4 |
| Acid value (direct) | 130–158 |
| Ester value | 42–69 |

Schmidt and Erban found :—

| | |
|---|---|
| Acid number | 136·3 |
| Saponification number | 164·7 |
| Iodine number | 57·4 |

and Williams gives the following figures :—

| | |
|---|---|
| Acid value (direct) | 98·0 |
| Saponification value (hot) | 148·4 |
| Iodine value | 76·45 |
| Loss at 100° | 4·66 |

Mills and Muter found the saponification value 223 and bromine value 38·9.

The author has recently made a thorough examination

of the various benzoins, and has elaborated the following methods for dealing with the natural drugs instead of extracts :—

I. *Determination of ash.*

II. *Acid value* (indirect).

One grm. of Siam benzoin, taken from a large average sample of the finely powdered drug, is treated in a flask with 10 c.c. of alcoholic $\frac{n}{2}$ potash and 50 c.c. of 96 per cent. alcohol for exactly five minutes, and then titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein until a single drop of the indicator no longer assumes a red coloration when introduced, and until the precipitated salts rapidly and completely subside. The supernatant liquid should be of a pure yellow colour. The volume (c.c.) of combined alkali multiplied by 28·08 gives the indirect acid value.

III. *Saponification value* (cold).

One grm. of Siam benzoin taken, as before, from an average sample, is placed in a stoppered flask, and mixed with 20 c.c. of alcoholic $\frac{n}{2}$ potash and 50 c.c. of benzine (sp. gr. 0·700). After leaving the closed flask for twenty-four hours at room temperature, the contents are diluted with alcohol and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The number of c.c. of combined KHO multiplied by 28·08 gives the cold saponification value.

IV. The *ester value* is found by subtracting the above acid value from the saponification value.

The following constants, etc., are given as characteristic of Siam benzoin, examined by the author's method :—

Ash = 0·03–1·50 per cent.

Solubility in alcohol should be complete except for a minute vegetable residue, 5 per cent. being the highest permissible limit.

Acid value (indirect) = 140–170.

Ester value = 50–75.

Saponification value (cold) = 220–240.

The author also examined the influence of various adulterants, *e. g.* colophony, dammar, storax, and turpentine, on these normal values, with the result that dammar was found to depress the acid value, turpentine the ester and saponification values, and storax the acid value; colophony, however, was difficult to detect, except when present in large quantities. The melting point and solubility in alcohol will also afford useful aid in this connection.

Finally, it may be mentioned that the following methoxyl values were obtained from Siam benzoin by Gregor and Bamberger :—

| | Gregor. | Bamberger. |
|---|---|---|
| Methoxyl value . . . | 43·4 | 30·0 |
| Do. . . . | 43·0 | 28·5 |

(As to the value of these figures compare *Chem. Rev.*, 1898, No. 10; and on the German Pharmacopœia tests for Siam benzoin, see *Ph. C.*, 1898, No. 20).

## 18. Sumatra Benzoin.

**Origin and Habitat.**—*Styrax Benzoin* (Styraceæ). Sumatra.

**Chemical Constituents.**—Ash, 0·01 per cent.; free benzoic acid; styrol ($C_8H_8$); traces of benzaldehyde ($C_6H_5CH$); benzol ($C_6H_6$); vanillin ($C_8H_8O_3$), 1 per cent.; cinnamic phenylpropyl ester ($C_{18}H_{18}O_2$), about 1 per cent.; cinnamocinnamic ester = styracin ($C_{18}H_{19}O_4C_9H_7O$), about 2–3 per cent.; cinnamic benzoresinol ester ($C_{16}H_{25}O_2C_9H_7O$), 7·4 per cent., and cinnamic benzoresinotannol ester 92·6 per cent. of the total esters—this ester mixture is the main component of Sumatra benzoin, the cinnamates amounting in the aggregate to 75 per cent. and yielding 24 per cent. of cinnamic acid. The isolated alcohols

have the formulæ—benzoresinol (crystalline) = $C_{16}H_{26}O_2$, and benzoresinotannol (amorphous) = $C_{18}H_{20}O_4$. The impurities amount to about 14–17 per cent (Tschirch & Lüdy).

**General Properties and Commercial Varieties.**—See Siam benzoin, as also for **Adulterants.**

**Analysis :—**

The solubility according to Hirschsohn is as follows :—

| | Per cent. soluble in Petroleum Ether— Dried at 17° C. | at 120° C. |
|---|---|---|
| Sumatra benzoin . . . | 12·06 | 4·48 |
| Do. . . . | 7·70 | 2·06 |
| Do. . . . | 4·90 | 3·64 |
| Do. . . . | 9·83 | 2·98 |

A. Kremel obtained the following values, using an extract :—

| | |
|---|---|
| Acid value (direct) . . . . . | 96·0 |
| Ester value . . . . . | 60·9 |
| Saponification value (hot) . . . . | 156·9 |

As in the case of Siam benzoin (*q.v.*) these figures are only of relative value.

Beckurts and Brüche found—

| | | |
|---|---|---|
| | Sp. gr. . . . . | 1·120–1·171 |
| | Ash . . . . . | ·05–2·38 % |
| | Insoluble in alcohol . . . | 2·1–9 % |
| From extract | Acid value (direct) . . . . | 97–132 |
| | Ester value . . . . . | 48–65 |
| | Saponification value (hot) . . | 160–188 |

The last three values, like those found by Kremel, having been obtained from extracts, are not to be relied on as representing the natural product.

E. Dieterich gives the following results :—

| | | |
|---|---|---|
| From extract | Acid value (direct) | 93·76–186·60 |
| | Ester value | 29·40–170·80 |
| | Saponification value (hot) | 160·64–265·05 |
| | Moisture | 4·00–8·20 |
| | Ash | 0·57–1·23 % |
| | Soluble in 96 per cent. alcohol | 68·09–85·80 % |

The above remarks apply also to the first three values on this list.

E. J. Parry has examined several samples of Sumatra benzoin, with the following results :—

| | |
|---|---|
| Mineral matter | 0·4–1·96 |
| Soluble in alcohol | 90–93·5 |
| Acid value | 98–139 |
| Ester value | 51–98 |

By the method described on p. 151 the author obtained the following values :—

| | |
|---|---|
| Acid value (indirect) | 100–130 |
| Ester value | 65–125 |
| Saponification value (cold) | 180–230 |
| Soluble in 96 per cent. alcohol | 78–80 % |
| Ash | 0·0–1·5 % |

all from the natural drug, and not—as those obtained by Kremel, Beckurts and Brüche, and E. Dieterich—from extracts which do not correspond to the natural product.

The author, in this case also, examined the influence of adulterants on these normal values, and arrived at conclusions similar to those already stated in the case of Siam benzoin (*q.v.*).

Evans' found 10·10–10·67 per cent. of matters insoluble in alcohol.

Some samples of benzoin contain, in addition to benzoic acid, more or less cinnamic acid, which is stated to be more

in evidence in the tears: thus Kolbe and Lautermann separated from the tears an acid which at first was thought to be peculiar, but this was subsequently proved to be a mixture of benzoic and cinnamic acids. Hermann Aschoff, operating on a sample of Sumatra benzoin, obtained pure cinnamic acid only, but H. Beckurts and W. Brüche have proved that this acid is absent from Siam benzoin. Tschirch and Lüdy confirmed the absence of cinnamic acid in the case of Siam benzoin and its presence in the Sumatra variety (see p. 149).

Gregor and Bamberger found the following methoxyl values :—

| | |
|---|---|
| Gregor . . . . . | 20·0–25·5 |
| Bamberger . . . . . | 13·0–16·5 |

The presence of cinnamic acid in benzoin can be readily demonstrated by heating with a little caustic soda solution, filtering and heating the filtrate with potassium permanganate, when an odour of bitter almonds is developed.

The detection of colophony by the Storch-Morawski reaction is described under " Colophony."

## 19. Palembang Benzoin.

**Origin and Habitat.**—Not from *Styrax Benzoin*, but from other *Styraceæ*, still unidentified, grown in farther India.

**Chemical Constituents.**—Impurities, 7·5 per cent.; no cinnamic acid, but benzoic acid and resin, 90–95 per cent. (Fr. Lüdy).

**General Properties, Commercial Varieties, Adulterants, etc.**—See Siam benzoin.

**Analysis :—**

Beckurts and Brüche found—

| | | |
|---|---|---|
| | Sp. gr. | 1·131 |
| | Ash | 2·38 % |
| | Insoluble in alcohol | 9·00 % |
| From extract | Acid value (direct) | 97 |
| | Ester value | 71 |
| | Saponification value (hot) | 168 |

The last three values have therefore merely a relative importance.

Parry's results are as follows—

| | |
|---|---|
| Sp. gr. | 1·1397–1·4100 |
| Insoluble in alcohol | 8·9–16·8 |
| Acid value | 96–121 |
| Ester value | 54–69 |

The author has examined natural Palembang benzoin by the method described on p. 151 and obtained the following values—

| | |
|---|---|
| Acid value (indirect) | 113·40–130·90 |
| Ester value | 84·0–91·0 |
| Saponification value (cold) | 198·0–219·80 |
| Ash | 1·101–4·023 % |

A sample of benzoin from the Federated Malay States examined at the Imperial Institute and classed as equal to Palembang gave—

| | |
|---|---|
| Moisture | 1·61 per cent. |
| Ash | 0·41 „ |
| Soluble in alcohol | 91·48 „ |

## 20. Padang Benzoin.

Nothing is definitely known regarding the origin and chemical composition of this variety, except that, like Siam and Palembang benzoin, it is free from cinnamic acid (K. Dieterich).

For the general properties, commercial varieties, adulterants, etc., see Siam benzoin.

**Analysis.**—The author has examined the natural drug by the method, already described, and found—

| | |
|---|---|
| Acid value (indirect) | 121·80–124·60 |
| Ester value | 79·80–81·20 |
| Saponification value (cold) | 201·60–205·80 |
| Ash | 1·070 % |

## 21. Penang Benzoin.

**Origin and Habitat.**—Probably obtained from *Styrax subdenticulata*, Mic. (Styraceæ). Further India.

**Chemical Constituents.**—Benzoic acid, cinnamic acid, and resin ester (Fr. Lüdy).

For the general properties, commercial varieties, adulterants, etc., see Siam benzoin.

**Analysis.**—A. Kremel found the following values (from an extract) :—

| | |
|---|---|
| Acid value (direct) | 122·2 |
| Ester value | 57·9 |
| Saponification value (hot) | 180·1 |

For reasons already mentioned, these figures possess nothing more than a merely relative value.

Evans found up to 6·17 per cent. of matters insoluble in alcohol.

The author subjected specimens of this variety to the method described on p. 151, and obtained the following results :—

| | |
|---|---|
| Acid value (indirect) | 121·80–137·20 |
| Ester value | 87·50–91·70 |
| Saponification value (cold) | 210·00–296·80 |
| Ash | 0·380–0·773 % |

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## 22. Caranna Resin.

*Resina Caranna.*

**Origin and Habitat.**—*Icica* and *Amyris Caranna* and *Bursera acuminata* (Burseraceæ). Antilles.

**Chemical Constituents.**—Not yet closely examined, but similar in composition to elemi.

**General Properties and Commercial Varieties.**—Dense, lustrous, brownish green, resinous masses, mostly wrapped in leaves; it is easily softened by heat, has a balsamic odour, and is to a large extent soluble in alcohol and ether. Employed to adulterate elemi (*q.v.*), with which it is often classified as an allied species. At present only rarely met with in commerce.

*Protium Caranna* (Burseraceæ), from Brazil, also yields a "Balsamo de Caranna," which, like other Protium elemis (Amessega, etc.), is allied to true elemi.

Antilles Caranna resin is also considered by some as identical with Bourbon Tacamahac, from *Calophyllum Tacamahaca* (*q.v.*, as also under elemi); and, in any case, it must be regarded as similar to elemi.

**Adulterants.**—Vegetable impurities.

**Analysis.**—Although this resin is rarely met with in commerce, it is of interest because it is used as an adulterant or surrogate of elemi. The product now in the market appears to be an artificial product.

Hirschsohn examined eleven kinds of Caranna resin, all of which, except two, he found to be completely soluble in alcohol, ether, or a mixture of both. The author has examined specimens of this resin, but cannot confirm Hirschsohn's opinion that it is identical with Bourbon Tacamahac (*q. v.*).

Examined by the usual method, Caranna resin from the Antilles yielded in the author's hands the following values :—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . . | 79·37 | 79·37 |
| Ester value . . . . | 110·48 | 111·84 |
| Saponification value (hot) . . | 189·85 | 191·21 |

Judging from these figures, Caranna does not appear to resemble elemi very closely, since the latter furnishes much lower values.

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K. Dieterich, Ph. C., 1889, No. 30.—Hirschsohn, A. d. Ph. 211, p. 253.

## 23. Colophony.

*Colophonium* (officinal in German Pharmacopœia).

**Origin and Habitat.**—Various species of *Pinus*. Europe. Colophony is the anhydrous residue from the distillation of the turpentine obtained from different trees of the *Pinus* family, especially *P. Laricio*, *P. Pinaster*, *P. Australis*, *P. Tœda*, and many others.

**Chemical Constituents.**—Chiefly abietic anhydride ($C_{44}H_{62}O_4$), with smaller quantities of acids allied to, isomeric,

or polymeric with abietic acid. (Abietic acid has the formula $C_{44}H_{64}O_5$ and is dibasic.) Also inert substances, pyrocatechuic acid, bitter principles, and slight traces of mineral constituents. No esters or their derivatives have been found, only resin acids, ethers, and lactones (the last-named according to Henriques). Jean isolated two other resinous constituents, and Lewkowitsch has indicated the presence of unsaponifiable hydrocarbons.

W. Schkateloff is of opinion that in such products as colophony, galipot, resinous saps, etc., the same acid is present, *i. e.* sylvic acid, but that it exists in three isomeric modifications. (1) $\alpha$-sylvic acid, crystallising in three-sided plates, having a melting point of 143°–144°, and the specific rotation $[a]_D + 73{\cdot}67°$; (2) $\beta$-sylvic acid, crystallising in three-sided plates, melting point 160° $[a]_D - 92{\cdot}5°$; and (3) $\gamma$-sylvic acid, crystallising in fine needles or three-sided plates, melting point 179°–180°, and optically inactive. The various acids which have been described by other observers may be regarded as belonging to one or other of these categories: thus the abietic acid described by Mack and Levy is probably identical with $\beta$-sylvic acid, and the pyromaric acid of Laurents is probably $\gamma$-sylvic acid.

Accompanying the three isomeric acids above mentioned, in all crude products there was found a yellow, uncrystallisable resin, referred to by Unverdorben as pinic acid, which appeared to have been produced by oxidation. From experimental observation it is regarded as probable that the formula of the resin acid is $C_{20}H_{28}O_2,\frac{1}{2}H_2O$; they are unsaturated compounds containing two double bonds. The difficulty of investigating the resinous products is referred to, and as an illustration it is stated that $\alpha$-sylvic acid from *Pinus sylvestris*, when melted, yielded a colophony with $[a]_D - 73{\cdot}5°$, that of *P. abies excelsa* gave a colophony with $[a]_D - 74{\cdot}1°$; this on heating at 170° became $[a]_D - 60°$, which

on further heating at 180°–190° was reduced to −18°, and finally it became inactive.

H. Mack has investigated the pure sylvic acid obtained by Maly's method, and also that of Flückiger; the former consisting in separating the soluble matters from colophony by long digestion with 70 per cent. alcohol and then recrystallising as many as thirty times from 90 per cent. alcohol. Prepared in this way the sylvic acid appeared as a pure white product, softening at 148° and melting at 153°–154°. The substance prepared by Flückiger's method, *i.e.* dissolving in absolute alcohol, precipitating with a current of hydrochloric acid gas, and recrystallising four times from methyl alcohol, was practically identical with the above in composition. From the figures obtained on combustion, the formula $C_{19}H_{28}O_2$ was calculated, this being confirmed by determinations of the molecular weight by Raoult's method when glacial acetic acid was used as a solvent.

A. Tschirch and B. Studer found the following constituents in a sample of American colophony, sp. gr. 1·090 at 15°: $\alpha$-abietinic acid ($C_{19}H_{28}O_2$), 30 per cent.; $\beta$-abietinic acid, 22 per cent.; $\gamma$-abietinic acid, 31·06 per cent.; volatile oil, 0·4 to 0·7 per cent.; resene 5 to 6 per cent. They also point out that the solubility of colophony decreases with age; thus one gram of fresh-powdered rosin required 60 c.c. of petroleum ether for solution, whereas one gram of old-powdered rosin required 400 c.c.; $\alpha$-abietinic acid required 500 c.c., $\beta$-abietinic acid 100 c.c., $\gamma$-abietinic acid 100 c.c., and the resene 50 c.c. per 1 grm. of material.

**General Properties and Commercial Varieties.**—The colophonies form pale, nearly white to dark brown-red, and in any case almost transparent, masses; brittle, with a vitreous lustre, and furnishing a nearly white powder; they soften in the hand, and are completely soluble in hot alcohol. Sp. gr. 1·070–1·080. The different grades are due

to difference in the mode of heating—short and gentle, or prolonged and intense—employed in the preparation.

Whereas the paler kinds are considered more valuable, and more suitable for pharmaceutical purposes, other consumers prefer the dark-coloured sorts; the colour is therefore not a criterion of suitability for any particular purpose, although a higher price is paid for the paler varieties.

**Adulterants.**—Owing to the low price of colophony, the only impurities likely to be present are merely of a mechanical character (chips of wood, dust, dirt, etc.), the more so because colophony itself forms a favourite adulterant for dammar, guaiacum, dragon's-blood, storax, benzoin, etc.

**Analysis.**—The detection of colophony and pine resin in pale resins can be effected by the Storch-Morawski reaction. The author, however, considers that it would be risky to form a definite opinion on the basis of this colour reaction alone, since various other resins, when dissolved in acetic acid, also give a red coloration on the addition of sulphuric acid; and because this reaction is so general and far from specific that it cannot lay claim to any particular value, whilst for dark coloured resins it is altogether unsuitable.

Hitherto it has been the general practice to take the presence of esters in colophony for granted, and to determine the ester value, saponification value, and ether value, as well as the sp. gr., solubility, ash, and acid value; but in the present state of knowledge with regard to the constituents of colophony, the ester and saponification value, and "unsaponifiable matter" determinations cannot be justified. The author, with a view to the introduction of uniformity in testing, has therefore proposed that only the sp. gr., ash, acid value, and degree of solubility should be determined.

Recently, Henriques—working on different lines to those previously followed by the author—has also succeeded in demonstrating the absence of esters. He has, however,

found ethers and lactones, which apparently justify an "ether value" or "constant ether value," though not the so-called ester values hitherto ascribed to colophony.

The following values have been found by different authors :—

A. Kremel obtained—

| | Pale. | Dark. | American. | English. |
|---|---|---|---|---|
| Acid value (direct) . . | 163·2 | 151·1 | 173·0 | 169·1 |

by dissolving the samples in alcohol and titrating direct with alkali.

The circumstance observed by Williams that the acid value increased with the purity of the sample, was probably due to the nature of impurities present and the small percentage of undecomposed abietic anhydride. He found—

| | |
|---|---|
| Loss at 100° . . . | 0·13–0·34 per cent. |
| Ash . . . . . | 0·02–1·20 ,, |
| Acid value . . . . | 166·6–179·2 |
| Saponification value . . | 176·4–195·7 |
| Iodine value . . . | 112·01–115·31 |

Von Schmidt and Erban give the following particulars with regard to solubility and also the usual constants as determined by them.

In Alcohol, Ether, Methyl alcohol, Amyl alcohol, Benzol } complete.

Petroleum ether—almost complete.

Acetone, Glacial acetic acid, Chloroform, Carbon di-sulphide, Oil of turpentine } complete.

| | |
|---|---|
| Acid value (direct) . . . . | 146·0–146·5 |
| Saponification value (hot) . . | 167·1–168·2 |
| Ether value . . . . . | 21·1 |
| Iodine value . . . . . | 116·8 |

E. Dieterich found—

| | |
|---|---|
| Acid value (direct) . . . . | 151·70–176·70 |
| Sp. gr. . . . . | 1·071–1·083 |

Mills and Muter found the saponification value of a sample of the refined rosin to be 181 and the iodine value 112·7, while A. Rudling gives the following figures :—

| | Water. | Substance Insoluble in Alcohol. | Acid Value. | Saponification Value. | Iodine Value. |
|---|---|---|---|---|---|
| White French rosin . . . | 0·80 | 0·10 | 169·7 | 177·8 | 137·1 |
| American rosin . . . | 0·75 | 0·20 | 157·9 | 182·0 | 122·0 |

Schmidt and Erban, after twenty-four hours' action with Hubl's solution, found the iodine value of colophony to be 116·8; Worstall, using large excess of iodine, found 170; and Parry, with the same process, gives the average figure as 125. By the Wijs process Ingle found, after acting half to one hour, the iodine value 150; while Langmuir and White, after one hour's action, obtained much higher figures, viz. 175·7 to 262·5.

Beckurts and Brüche found—

| | Red. | White. | Yellow. | Brown. |
|---|---|---|---|---|
| Sp. gr. . . . | 1·071–1·080 | 1·068 | 1·067 | 1·081 |
| Acid value (direct) . | 173–186 | 180 | 185 | 181 |
| Ether value . . . | 0–12 | 0 | 0 | 0 |
| Sapon. value (hot) . | 179–193 | 180 | 185 | 181 |

The term "ether" value has been used in this place instead of "ester" value, the researches of the author and Henriques having shown it to be more suitable.

On the basis of his own experiments and numerous previously published values,[1] the author proposes the following method of examination :—

[1] *H. A.*, 1896, 1897, *sub.* "Colophonium."

(*a*) *Sp. gr. determination.*—A series of solutions of common salt, ranging between sp. gr. 1·070 and 1·085 at 15° C., are prepared, and in each of these is placed a few fragments of the colophony under examination, the temperature being maintained constant. The sp. gr. of the solution which retains the colophony in suspension will be the same as that of the substance. In selecting the best pieces, care must be taken to reject any which exhibit cracks, air bubbles, or impurities.

The Mohr-Westphal balance can also be advantageously used for sp. gr. determinations, the usual method employed for beeswax [1] being pursued.

(*b*) *Acid value* (indirect).—One grm. of finely powdered colophony is treated with 25 c.c. of alcoholic $\frac{n}{2}$ potash and left covered up for two hours—or until such time as the whole is dissolved—after which it is titrated back with $\frac{n}{2}$ sulphuric acid. The number of c.c. of combined KHO multiplied by 28·08 gives the acid value (indirect). No water should be added upon any account, and the strength of the alkali should be controlled by a blank experiment, without colophony.

The author finds that direct titration usually gives lower values than the indirect method, and aqueous alkali lower results than either method with alcoholic alkali. The above reverse titration gives values approximating most nearly to those furnished by theoretical calculation, and, in addition, the necessity for preparing a solution beforehand is obviated, the alkali serving both as a solvent and for neutralising the acid. No water should be added, since this liquid brings about the dissociation of the rosin soap.

The author submits the following standard of requirements for determining the purity of colophony in a uniform

[1] *H. A.*, 1897, p. 362.

manner, it being remarked that for technical and pharmaceutical purposes certain other criteria are required, which, however, must be left to the domain of these special branches, being too divergent to deal with in describing a uniform method. For example, a very pale colophony is preferable for pharmaceutical purposes, whereas in certain technical processes colour plays no particular part.

" Colophony should be as light coloured as possible, and, when boiled with water and the extract tested with ferric chloride, should give only a minimum colour reaction. It should be almost entirely free from mineral matter and *completely* soluble in alcohol, ethereal oils, acetone, ether, chloroform, methyl alcohol, amyl alcohol, acetic ether, benzol, oil of turpentine, and carbon di-sulphide; also *partly* soluble in benzine, petroleum, and petroleum ether.

" The acid value when determined by the above indirect method should vary between 145 and 185, and the sp. gr. between 1·045 and 1·085."

The ether value, or Henrique's constant ether value can be determined by the " usual " hot saponification method (see Introduction to Pt. II.), subtracting the acid value from the resulting saponification value.

Fahrion[1] has shown the untenability of the author's standard of 7 per cent. as the maximum percentage of matters insoluble in petroleum ether, it being found that a few good commercial sorts of colophony exhibit a larger amount of insoluble residue. This is confirmed by C. Schwalbe, who states that rosin changes on exposure to light and air, thus becoming insoluble in petroleum ether. The " weathered " crust from rosin may contain as much as 70 per cent. insoluble in this solvent. The oxygen-absorption of colophony has been dealt with by Weger, in his treatise already cited.

[1] *Zeitschrift f. angewandte Chemie*, 1898, No. 34.

Kitt found the carbonyl value = 0·54–0·56.

Gregor and Bamberger obtained negative results in the methoyxl value test.

The following acetyl values were found by the author :—

| | | |
|---|---|---|
| Acetyl | Acid value . . . . | 155·82–155·84 |
| | Ester value . . . . | 92·12–95·37 |
| | Saponification value . . | 251·21–274·94 |

The worth of these values was discussed in *Chem. Rev.*, 1898, No. 10; and the German Pharmacopœia tests for colophony were dealt with by the author in *Ph. C.*, 1898, No. 20.

As already mentioned, a discussion has been carried on by the author, Fahrion, Schick, and Heupel,[1] with regard to the determination of the acid, ester, ether, and saponification values. The author, on the basis of his researches, held colophony to be free from esters, and therefore incapable of having any ester value.

Henriques confirmed the absence of esters by other means, and recommended the direct estimation of the acid value and the determination of a "constant ether value," because he succeeded in showing the presence of ethers and lactones in colophony. These discoveries terminated, in some respects, the debatable colophony question, since all that is necessary, in the absence of esters, is to rechristen the ester value (advocated by Schick, Fahrion, and Heupel) by the name "ether value," in order to annul the previously existing chemical contradiction first exposed by the author. For this reason all the corresponding values have here been termed "ether values."

The colophony from India has been examined at the laboratories of the Imperial Institute, the results agreeing

[1] *Zeits. f. angew. Chem.*, 1898, Nos. 12, 14, 17, 19; 1899, Nos. 2, 5, 8, 12.

fairly closely with those of American and French rosin. The results are given below :—

| Source. | *Pinus longifolia* (Naini Tal). 1. | 2. | Natural Turpentine (Naini Tal). | *Pinus excelsa* (Punjab). | *Pinus Gerardiana* (Punjab). |
|---|---|---|---|---|---|
| Melting point . . | 75°–85° | 74° | — | — | — |
| Specific gravity . . | 1·067 | — | — | — | — |
| Ash, per cent. . . | 0·125 | 0·15 | — | — | — |
| Acid value . . . | 165·0 | 174 | 170·1 | 170·0 | 174·0 |
| Saponification value . | 190·0 | 184 | 193·0 | 194·0 | 176·0 |
| Unsaponifiable, per cent. | 5·0 | — | 3·8 | 9·0 | 6·9 |
| Specific rotation . . | + 9° 40′ | — | *Nil* | − 4° 48′ | + 11° 20′ |
| Moisture . . . | — | 0·80 | — | — | — |

P. Foester (*Ann. Chim. Analyt.*, 1909, p. 14) suggested the use of Halphen's reagent for detecting colophony in admixture with other resins. This reagent consists of (A) 1 part by volume of phenol dissolved in 2 parts of carbon tetrachloride, (B) 1 pt. of bromine in 4 parts of carbon tetrachloride. The test consists in adding to the substance to be examined 2 c.c. of solution A and then bringing some of solution B into close proximity to it, when a bright blue colour, changing to violet, occurs if colophony is present. Shellac is tested by treating 2 grms. of the resin, which has been powdered along with a little sand, with 10 to 15 c.c. of ether, evaporating the solution and testing the residue. Jalap resin is extracted with a little petroleum spirit which is evaporated off and the residue tested. Guaiacum resin can also be detected by using acetic acid or acetic anhydride for dissolving and submitting the solution to the bromine vapour evolved from solution B, yielding a bright blue colour changing to green when the bromine is in excess.

The colour reactions of various resins with Halphen's reagent (bromine and phenol) have been investigated by E. F. Hicks (*J. Ind. Eng. Chem.*, 1911, p. 86). Colophony, as is well known, gives a violet colour; dammar yields a

brown changing to lilac brown; elemi an indigo blue which is permanent but becomes more violet on standing; kauri yields an azure-blue colour which changes very rapidly to violet and purple; Manila copal (soluble in spirit) at first assumes a faint brownish-green colour which changes slowly to violet, then purple; mastic gives a reddish-brown colour; sandarac yields a permanent violet colour; shellac when pure is not coloured; Zanzibar copal appears first of a light brown colour—this changes to brownish-violet and afterwards to a chocolate brown with a violet tint. The tests are applied to fairly concentrated solutions, and, as many of the resins are soluble in phenol, this may be used as the solvent. Water, alcohol, or ether should on no account be present to any considerable extent, as they render the tests less sensitive.

P. E. Jameson has drawn attention to the fact that other resins besides colophony yield colour reactions with the Liebermann-Storch test, and that unless care is taken the results are likely to be misleading. Thus kauri gives a deep red colour changing to brown; amber, East India and black dammar a deep wine-red changing to brown; Batavia and Borneo resins a deep wine-red colour which does not change, and some samples of Manila copal also give colours similar to that of colophony.

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## 24. Copal.

*Resina Copal.*

**Origin and Habitat.**—Certain species of *Trachylobium* and *Hymenæa* (Cæsalpinieæ) fossil, recent fossil, and recent resins. Africa, America, and East Indies.

**Chemical Constituents.**—Zanzibar copal is the only variety that has been carefully examined. It contains trachylolic acid ($C_{54}H_{85}O_3$ $OH(COOH)_2$), 80 per cent., (M.P. 168°); isotrachylolic acid ($C_{54}H_{85}O_3$ $OH(COOH)_2$), 4 per cent.; $\alpha$-copal resene ($C_{41}H_{86}O_4$), and $\beta$-copal resene ($C_{25}H_{38}O_4$), together 6 per cent.; impurities, 0·42 per cent.; ash, 0·12 per cent.; bitter principle and ethereal oil, 9·46 per cent. Trachylolic acid and its isomer are distinguishable by their different solubility, behaviour with lead acetate, and melting point (C. Stephan).

Tschirch (*Ph. Ztg.*, 1899, No. 77) has recently isolated new "crystalline resinolic acids" by fractional extraction.

**General Properties and Commercial Varieties.**—The name copal is a generic term. In England, anime is synonymous with copal (see Anime).

Copals vary in appearance according to whether they are in the crude, decorticated, or washed condition. They are nearly all more or less vitreous, transparent, yellow to red in colour, and with or without a faceted surface (goose skin), the latter being specially characteristic of Zanzibar copal. The following principal fossil, semi-fossil, and recent varieties have been identified:[1]—East African, West African, South American, East Indian, and Kaurie copal.

These larger classes may be subdivided into—

[1] See the treatises of Gilg, *Chem. Rev.*, 1898, Nos. 8, 9; Zucker, *Ph. Ztg.*, 1898, p. 848; *Dingler's Polyt. Journ.*, 1897, p. 212; Bocquillon, *Rép. de Pharm.*, series 3, vol. ix., 1897, No. 8; Wiesner's *Techn. verw. Bals.-Harze, Gummiharze*, 1869, pp. 144–168.

*East African.*—Zanzibar, probably from *Trachylobium mossambicense* or *Hymenæa verrucosa* (best and hardest kind, M.P. over 400° C.), Mozambique, Madagascar.

*West African.*—Young copal, from Sierra Leone; flint copal; Gaboon, Loango, Angola, Benguela, and Congo copal, from *Guibourtia copallifera* or species of Copaifera.

Benguela and Angola copal are known in commerce as "Ocota Cocota" and "Muccocota" gum.

*American.*—Courbaril copal (from *Hymenæa Courbaril*) and copal from other species of Hymenæa, such as *Hymenæa admirabilis, stilbocarpa*, etc., also known as "Anime" (*q.v.*).

*East Indian.*—Manila copal, from *Vateria Indica* (Dipterocarpeæ), also known as "white dammar" (*q.v.*).

*Kauri Copal*, from *Damara Australis* (Coniferæ), also known as "New Zealand dammar."

*White Zanzibar copal*, or Zanzibar copal in balls, is sold in Zanzibar as "tree copal"; it is of low quality, soft, and recent. "Chakazzi" copal mostly comes into commerce as "Zanzibar copal without goose skin."

As copal is frequently shipped to a distance for washing, Zanzibar copal has also been met with under the names "Salem" and "Bombay" copal, there being large copal-washing works in the United States, whilst a good deal of copal used to come on the market via Bombay.

For rare types of copal, such as Inhambane and Accra copal, see Gilg's treatise already cited. According to the latest researches of this worker, both Madagascar and Zanzibar copal are derived from the same tree, *Trachylobium verrucosum* (which is identical with *T. mossambicum*). They certainly exhibit many characteristics in common.

According to Wiesner, copals can be marked (scratched) by calcspar; some varieties—Sierra Leone, Gaboon, Angola—are of equal hardness with rock salt. Zanzibar and Mozam-

bique copal are between rock salt and copper sulphate in point of hardness; whilst Benguela, Kauri, and Manila copal are less hard than rock salt. The scale of hardness may therefore be arranged as follows:—(1) Zanzibar copal, (2) Mozambique, (3) Sierra Leone (flint copal), (4) Gaboon, (5) Angola, (6) Benguela, (7) Kauri, (8) Manila, and (9) Courbaril copal.

The East African copals are fossil, those from West Africa semi-fossil, the Kauri copals semi-fossil, the South American kinds recent; but nothing definite in this respect is known of the Indian copals.

According to Worlée, the " hard " copals are :—Zanzibar, Sierra Leone, Benguela, and Angola copal; the " soft " copals being—West Indian, ball Kauri, and Manila copal; whilst Zucker adds Accra copal to this latter class.

The copals are distinguished in commerce according to colour—white, pale, or dark red; condition—natural, half-shelled, or shelled; and other peculiarities. For the distinction between true copals and amber, or the resins from *Coniferæ* and *Dipterocarpeæ*, see under " Analysis."

**Adulterants.**—False, soft copals, coniferous and dipterocarpous resins and amber.

**Analysis.**—Of the unusually large number of copals, all of which are valued according to the degree of hardness and the corresponding insolubility in alcohol, but few analytical details are available. The solubility and fusibility vary with the origin and age, the melting points ranging from 180°–340° C., the hardest kinds being the most refractory. In alcohol the soft varieties are only partially soluble, the harder kinds scarcely at all. Rosemary oil and Cajuput oil dissolve nearly all copals, but not amber; and nearly all are soluble in oil of turpentine, at least after being melted or distilled—even such as were previously untouched by this

solvent—so that almost all are rendered completely soluble therein, or in fatty oils, etc., a property which is of high technical importance. Many copals, too, when they have been exposed for a long time to sunlight, and have absorbed oxygen, become soluble, or at least more soluble than before. According to Andres, the copals are soluble in strong (anhydrous) alcohol, provided they have previously been allowed to swell up in ether; mixtures of absolute alcohol and oil of turpentine are also said to form a good solvent for soft copals. Andres recommends a mixture of carbon di-sulphide, oil of turpentine, and benzol (equal parts) as the best solvent for unmelted, undistilled copal. To convert the copals into a soluble form, the usual practice is to heat them to 200°–220° C. for several days, or else distil them, dry (until twenty-five per cent. of copal oil, which is afterwards used as a solvent, has passed over)—the temperature employed being 380°–400° C. The copal is then soluble in oil of turpentine, the degree of solubility varying with the amount of copal oil distilled over.

The following table compiled by Violette shows the results furnished by 100 grms. of copal :—

| Loss of Weight on Distillation. | Amount of Oil Collected. | Behaviour of the Distilled Copal in Presence of Oil of Turpentine. |
|---|---|---|
| Grms. | Grms. | |
| 3·0 | 3·0 | Insoluble |
| 9·0 | 8·5 | Do. |
| 10·5 | 10·2 | Do. |
| 16·0 | 15·7 | Do. |
| 20·0 | 19·0 | Somewhat soluble |
| 22·0 | 21·3 | More readily soluble |
| 25·0 | 24·5 | Very readily soluble |
| 28·0 | 27·1 | Do. do. |
| 30·0 | 29·0 | Do. do. |
| 32·0 | 31·0 | Do. do. |

In practice usually only about 10–12 per cent. is distilled off.

Both copal oil and amber oil are employed for dissolving soft grades of copal.

What the copals and ambers gain in solubility by distillation they lose in point of colour, *i. e.* they become darker in proportion to the temperature or time of heating. It may also be mentioned that the copals are used for the preparation of lacquer varnishes (solutions of melted copal in linseed oil varnish) and ordinary lacquers (resin solutions without varnish).

The sp. gr. is given by Meichel and Stingel as 1·062–1·149, and by Brisson as 1·045–1·390. Tables have been drawn up for the differentiation of hard and soft copals, but though the data—like those given by older authors (Dierbach, Perrolet, Hanbury, Daniell, Gisecke, Lindemann, Wachsmuth, Jonas, Constantini, Böttger, Heeren, and others)—contribute to some extent to the characterisation of the copals, they are not as a rule directly useful, being in many cases contradictory.

Williams determined the loss of weight at 100° C. in a number of specimens and found it to range between 0·57–2·41 per cent., and the ash 0·27–2·06 per cent., with the following other values by the usual method :—

| Copal. | Acid Value (direct). | Ester Value. | Sapon. Value (hot). | Iodine Value. |
|---|---|---|---|---|
| Manila . . . . | 131·6 | 53·5 | 184·1 | 137·79 |
| Borneo . . . . | 141·4 | 35·3 | 176·7 | 138·04 |
| Singapore . . . | 128·8 | 65·3 | 194·1 | 123·31 |
| Sierra Leone . . . | 84·0 | 45·0 | 129·0 | 138·04 |
| Red Sierra Leone . . | 72·8 | 65·7 | 138·5 | 133·35 |
| Red Accra . . . | 46·2 | 85·4 | 131·6 | 121·66 |
| White Angola . . | 57·4 | 75·6 | 133·0 | 129·66 |
| Red Angola . . . | 60·2 | 76·0 | 136·2 | 136·90 |

As the true copals, such as Zanzibar copal, have been found to contain no esters, the above ester and saponification

Von SCHMIDT and ERBAN give the following Solubilities :—

| Copal. | Alcohol. | Ether. | Methyl Alcohol. | Amyl Alcohol. | Benzol. | Petroleum ether. | Acetone. | Glacial Acetic Acid. | Chloro-form. | Carbon di-sulphide. | Oil of Turpentine. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **I. Natural.** | | | | | | | | | | | |
| Zanzibar | insol. | partly sol. | insol. | sparingly sol. | partly sol. | insol. | insol. | partly sol. | partly sol. | insol. | partly sol. |
| Red Angola | insol. | partly sol. | partly sol. | sol. | partly sol. | partly sol. | partly sol. | partly sol. | partly sol. | almost sol. | partly sol. |
| White do. | insol. | partly sol. | insol. | partly sol. | partly sol. | insol. | insol. | partly sol. | partly sol. | almost sol. | almost insol. |
| **II. Shelled.** | | | | | | | | | | | |
| Zanzibar | almost sol. | partly sol. | insol. | partly sol. | almost com-pletely sol. | insol. | almost sol. | partly sol. | partly sol. | nearly sol. | almost completely sol. |
| Red Angola | partly sol. | almost com-pletely sol. | sparingly sol. | sol. | partly sol. | almost insol. | sparingly sol. | partly sol. | sol. | nearly sol. | almost completely sol. |
| White do. | partly sol. | partly sol. | sparingly sol. | partly sol. | partly sol. | almost insol. | almost insol. | partly sol. | partly sol. | nearly sol. | almost completely sol. |

values must be accepted with some reserve, the more so because the dipterocarpous resins (such as Manila copal from *Vateria Indica*) may also be free from esters, like the dammars.

According to Hirschsohn, petroleum ether dissolves only 6·5 per cent. of good African copal. Alcohol dissolves only 25 per cent. of the best copals; and the solubility in chloroform varies inversely with the hardness, 42 per cent. of best East Indian copal, 52 per cent. of African, and 46 per cent. of Angola copal being dissolved, whilst Kauri and Brazilian sorts are completely soluble.

Von Schmidt and Erban give the following values for copals :—

| Copal. | Acid Value (direct). | Ester Value. | Sapon. Value (hot). | Iodine Value. |
|---|---|---|---|---|
| Melted white Angola . | 93·6 | 25·2 | 118·8 | 44·9 |
| Melted red Angola . . | 30·5 | 89·2 | 119·7 | 34·8 |
| Unmelted red Angola . | — | — | 148·0 | — |
| Unmelted white Angola . | — | — | 132·2 | — |
| Unmelted Zanzibar . . | — | — | 92·4 | — |
| Melted Zanzibar . . | — | — | 36·8 | 12·6 |

which, however, do not agree with those found by Williams.

Mills and Muter found for a sample of copal the saponification value 124 and bromine value 89·9.

Special mention should be made of Friedburg's studies on copal resins. He states that hard copal is insoluble in alcohol, ether, and oil of turpentine, though it dissolves in the two latter after having been heated. When heated to a temperature of about 182° C. the copal, although showing no signs of decomposition, forms, on cooling, a highly lustrous, vitreous, translucent resin, readily soluble in cold or warm oil of turpentine. Copal is soluble in aniline and its homologues, as also in nitrobenzol and chloroform; phenol and cymol likewise form good solvents for copal.

Benzaldehyde dissolves copal completely at first, but soon the mass thickens (owing to the condensation of resin acids, etc., with aldehydes ?). Glacial acetic acid partly dissolves copal; and carbon di-sulphide is taken up in large amount, forming a colloid which becomes brittle on drying. According to Friedburg there are three classes of copals—soft, semi-hard, and hard. With regard to the solubility of copal in chloral hydrate (see below), mention may also be made of Fleming's discovery of the solubility of copal in epi- and di-chlorhydrin, which he has patented. Valenta recommends such solutions of copal or other resins as a coating for supporting the emulsion on photographic negatives.

For distinguishing true copals from coniferous and dipterocarpous resins, Mauch recommends the chloral hydrate test—true copal being insoluble in an 80 per cent. solution of this reagent, whilst dammar, colophony, Kauri and Manila copal are either partially or completely soluble therein. Zucker proposes the following test for distinguishing hard copals from the soft varieties :—The sample is treated with boiling water, and left to stand for half an hour. Hard copal remains unaltered, but the soft kinds become milky and opaque.

With reference to the foregoing analytical data, it may be mentioned that the saponification values have also been determined, as well as the acid values, but are of merely relative worth, since we now know that the copals, both the true kinds and those resembling dammar, consist of only neutral bodies and resin acids, and are free from esters. These conditions have already been referred to by Kremel, who also gives for copal (which he calls dammar) from *Vateria Indica* the acid value 15·4, while for the other copals he gives 127–147. The author recently examined Zanzibar copal, and found that direct titration gives unduly low

results; that an addition of water decomposes the resin soap; that existing values are unreliable; and that indirect titration is the best method of determining the acid value in copal. Already, in the case of dammar, sandarach, etc., he found that titration in an alcoholic liquid gave unreliable and irregular acid values, owing to the fact that the resinolic acids are not so easily or rapidly neutralised by the alkali, and, consequently, they are best treated by the indirect titration method. With Zanzibar copal similar conditions prevail, the neutralisation being so slow that it does not yield reliable values when the copal is dissolved in ether-alcohol, as practised by Kremel. By the direct method, he found the acid value to be 15–20, whilst Kremel, working in the same manner, gives 130–150, which must either be a printer's error for 13–15, or an error due to some defect in the titration; and, in fact, the author's experiments on this point indicate the use of water as the source of the discrepancy. Kremel added water to dissolve the salts during titration, an erroneous procedure, since it causes the decomposition of the resin soap. If the titration be completed without water, and then some of that liquid added, the red coloration at once vanishes, a sign that the water has decomposed the resin soap and that secondary reactions have occurred.

In the same manner, an addition of water at the end of the indirect titration process will eliminate the red coloration, thus indicating the fixation of alkali. The difference in the consumption of alkali when working with and without water may amount to as much as 2 c.c., which probably explains the excessively high values given by Kremel; in fact, the deficit, due to insufficient combination with the resin acids, in the direct titration method employed by Kremel was converted into an excess by the secondary reactions ensuing on the addition of water.

The author proceeds on the following lines :—

*Acid value* (indirect).—One grm. of finely pulverised Zanzibar copal is placed in a glass-stoppered flask and mixed with 25 c.c. of benzine, 25 c.c. of ether, and 20 c.c. of alcoholic $\frac{n}{2}$ potash. The closed flask is left at room temperature for twenty-four hours, and the contents are then titrated with $\frac{n}{2}$ sulphuric acid and phenolphthalein, without any addition of water.

The resulting acid value is, in the case of Zanzibar copal, between 60 and 65.

Intermediate members between the copals and the dammars and Kauri copal, as well as adulterations with amber, may be detected by the relative solubilities and behaviour with chloral hydrate, as also by their behaviour towards Cajuput oil, and their abnormal acid values. Moreover, amber gives ester and saponification values, copal only the indirect acid value (see also Amber, and Kremel's paper on Copal and Amber, in *N. z. P. d. A.*, 1889).

The acetyl, carbonyl, and methoxyl values of Zanzibar copal have also been determined recently, the author finding—

| Zanzibar Copal. | Acetyl. | | |
|---|---|---|---|
| | Acid Value. | Ester Value. | Saponification Value. |
| Soluble portion | 77·71 | 125·58 | 203·29 |
| Insoluble portion | 210·10–221·14 | 84·80–111·17 | 305·94–331·27 |

Kitt found, for East Indian copal, the carbonyl value 0·61; and Gregor and Bamberger both obtained negative results with the methoxyl test. (For the worth of these values, see *Chem. Rev.*, 1898, p. 10.)

The so-called "ester resins" serving as competitors of, and substitutes for, copal have been described by Zucker (*Ph. Ztg.*, 1898, p. 848).

The melting points of the different copals as given by several authors vary so much that it appears doubtful whether they were always dealing with authenticated samples. The following figures are given by Bottler :—

| | Melting Point. | Sp. gr. | Sp. gr. (usual figures). |
|---|---|---|---|
| Copal (Hymenæa). . . . | 90°–95° | 1·070 | 1·082 |
| Manila (yellow hard) . . . | 145° | 1·069 | 1·121–1·062 |
| Kauri . . . . . | 150° | 1·0456 | 1·050–1·109 |
| Benguela (yellow) . . . . | 180° | 1·065 | 1·062–1·081 |
| ,, (white) . . . . | 180° | 1·0593 | 1·062–1·081 |
| Congo . . . . . | 190° | 1·0480 | 1·062–1·081 |
| Sierra Leone . . . . | 195° | 1·064 | 1·06 |
| ,, (fossil pebble) . . | 230° | 1·067 | 1·09 |
| Angola (white) . . . . | 245° | 1·035 | 1·062–1·081 |
| Zanzibar . . . . . | 275° | 1·0621 | 1·068–1·067 |
| Angola (red) . . . . . | 315° | 1·068 | 1·081–1·064 |

According to M. Guédras, the fusing point of Madagascar copal is 150°, and acid value 143; Congo copal, M.P. 105°, acid value 35·55; Kauri copal, acid value 69·7.

C. Coffignier has determined the usual constants for several varieties of copal, the figures being produced below, also their solubilities in a large number of liquids, for which details see p. 36.

| | Specific Gravity. | Softening Point. | Melting Point. | Acid Value. | Sapon. Value. |
|---|---|---|---|---|---|
| Benguela . . | 1·058 at 16° | 65° | 165° | 123·1 | 157·1 |
| Angola (white) . | 1·055 at 17° | 45° | 95° | 127 | 159·9 |
| ,, (red) . . | 1·066 at 17° | 90° | 300° | 128·3 | 131·8 |
| Congo . . . | 1·061 at 17° | 90° | 195° | 132·3 | 131·8 |
| Sierra Leone . . | 1·072 at 19° | 60° | 130° | 110·2 | 123·4 |
| Kissel . . . | 1·066 at 27° | — | 110° | 70·4 | 117·8 |
| Cameroon . . | 1·052 at 27° | — | 150° | 159·7 | 170·0 |
| Accra . . . | 1·033 at 27° | — | 120° | 97·8 | 140·0 |
| Manila (hard) . | 1·065 at 17° | 80° | 190° | 72·8 | 87·0 |
| ,, (friable) . | 1·060 at 17° | 45° | 120° | 145·2 | 185·1 |
| Pontianak . . | 1·037 at 16° | 55° | 135° | 134·3 | 186·5 |
| Brazil . . . | — | — | 100° | 123 | 133·3 |
| Colombia . . | — | — | above 300° | 118·8 | 155·7 |

A new fossil copal from Java, examined by K. Dieterich, gave the following figures, the solubilities are also given in the original (*Chem. Centrl.*, 1905, ii, p. 1430):—

| | |
|---|---|
| Specific gravity | 1·033–1·041 |
| Softening point | 160°–170° |
| Melting point | 175° |
| Loss at 100° | 0·265 |
| Ash | 2·44 |
| Acid number | 4·55–5·07 |
| Saponification number | 14·54–18·03 |
| Ester number | 9·98–12·96 |
| Iodine number (Hubl-Waller) | 50·86–54·66 |

The following copals have been examined by R. A. Worstall:—

| | Iodine Value. | Acid Value. |
|---|---|---|
| Zanzibar, white sorts | 79 | 123 |
| ,, amber chips | 104 | 115 |
| Mozambique, white sorts | 80 | 136 |
| Madagascar | 95 | 126 |
| West African, North Coast, Akra, Red Angola, White Angola, Congo, Benguela | 122–143 | 108–152 |
| Sierra Leone | 114–118 | 102–105 |
| Brazilian | 123–134 | 131–149 |
| Kauri, lumps | 170 | 72 |
| ,, dust | 74 | 142 |
| Manila, large | 148 | 146 |
| ,, dust | 104 | 199 |
| Pontianak | 119–142 | 135–143 |
| Damar | 103–124 | 24–55 |

Sierra Leone, Kauri, Manila, and Pontianak resins were stated to be free from esters. The iodine value was estimated by the Hubl method, the time of action being eighteen hours.

According to A. Engel, Congo copal contains congocopalic acid ($C_{19}H_{30}O_2$, M.P. 115°–118°), 48–50 per cent.; congocopalolic acid ($C_{22}H_{33}O_4$, M.P. 108°–110°), 22 per cent.; $\alpha$-congocopalresene, 5–6 per cent.; $\beta$-congocopalresene (M.P. 175°–178°), 12 per cent.; ethereal oil, 3–4 per cent.; and impurities and ash, 4–5 per cent. Benguela copal contained bengucopalic acid ($C_{19}H_{30}O_2$, M.P. 134°–136°), 43–45 per cent.; bengucopalolic acid ($C_{21}H_{32}O_3$, M.P. 114°–116°), 22 per cent.; $\alpha$-bengucopalresene, 4–5 per cent.; $\beta$-bengucopalresene ($C_{22}H_{36}O_2$, M.P. 192°–196°), and ethereal oil, 3–4 per cent. All the above products were found to be amorphous.

Colombia copal has been examined by S. Machenbaum. This resin occurs in rather large pieces, some of which are pale coloured, others dark; the constants are given below :—

| | |
|---|---|
| Softening point | 120° |
| Melting point | 155° |
| Acid value (direct) | 105·0 |
| ,, ,, (indirect) | 106·12 |
| Saponification value (hot) | 110·60 |
| ,, ,, (cold) | 106·80 |

Examined by the method of Tschirch, it yielded four acids which were not named but the composition of which agree with the formulæ $C_{22}H_{40}O_3$, $C_{20}H_{40}O_2$, $C_{14}H_{24}O_2$, and $C_9H_{20}O_3$, and two resenes, one of which amounted to approximately 30 per cent., and 2 per cent. of ash.

S. Machenbaum has also examined a Brazilian copal, the figures for which are—

| | |
|---|---|
| Softening point | 127° |
| Melting point | 160° |
| Acid value (direct) | 123·2 |
| ,, ,, (indirect) | 128·56 |
| Saponification value (hot) | 144·24 |
| ,, ,, (cold) | 136·26 |

Further examination revealed the presence of three acids, $C_{24}H_{40}O_3$, $C_{22}H_{38}O_2$, and $C_{16}H_{30}O_2$, two resenes and an essential oil, and ash 4 per cent.

A sample of copal from Colombia has been examined at the Imperial Institute. It is known locally under the names "ambara" and "algarovilla," and is supposed to be derived from *Hymenæa splendida*. It was of a pale brown colour and was covered with a weathered crust :—

| | |
|---|---|
| Melting point | 123° C. |
| Acid value | 100·8 |
| Saponification value | 103·6 |

**Copals from Mozambique.**—Nine sample of copal resin were received at the laboratories of the Imperial Institute and were submitted to analysis with the following results. They were all collected from existing trees, the source being identified at Kew as *Copaifera Gorshiana* (Benth.).

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|---|---|---|---|---|---|---|---|---|---|
| Moisture | 1·35 | 0·82 | 1·63 | 0·7 | 0·93 | 0·32 | 0·47 | 1·64 | 1·13 |
| Ash | 0·55 | 0·04 | 0·73 | 0·3 | 0·6 | 0·26 | 0·35 | 5·40 | 1·52 |
| | | | | | | Approx. | | | |
| Melting point | 100° (approx.) | 92° | 105° | 87° | 81° | 105° | 105° | 124° | 105°–115° |
| Acid number | 95·5 | 73 | 138 | 115 | 126 | 132 | 128 | 156 | 115 |
| Sapon. number | — | — | — | 130 | 129 | — | — | — | — |

These were mostly completely soluble in a mixture of alcohol and benzene, also in a mixture of alcohol and turpentine, and partially soluble in alcohol, ether, chloroform, benzene, and turpentine.

**Copals from Ashanti, Gold Coast, Sierra Leone,**

**and Southern Nigeria.**—Copals from these sources have also been examined at the Imperial Institute, the results being as follows :—

| | Accra Copal from Ashanti. | | | | Accra Copal from Gold Coast. | | Sierra Leone | | Nigeria. | Ogea. |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1. | 2. | 3. | 4. | 1. | 2. | 1. | 2. | | |
| Ash . . | 0·1 | 2·21 | 0·12 | 0·5 | — | 0·2 | ·04 | 0·2 | 0 | 0·5 |
| Acid number | 124 | 134 | 133 | 126 | 133 | 133 | 127 | 127 | 110 | 116 |
| Melting point | 180° | 145° | 120° | 128° | — | — | 137° | 125° | 180° (approx.) | 120° (approx.) |
| Moisture . | — | — | — | — | — | 4·6 | — | — | — | — |

These copals are derived from trees which have been identified as a species of *Cyanothyrsus* and not from a species of Copaifera, as usually supposed. The Nigerian copal and Ogea gum are from *Cyanothyrsus Ogea* (Harms.), *Daniella oblonga* (Oliv.).

Tschirch and Rackwitz have examined both Angola and Cameroon copals, their results being as follows :—

| | M.P. | Acid Number. | Saponification Number. | Iodine Number. |
|---|---|---|---|---|
| Angola . . | 140°–170° | 135 | 155 | 66 |
| Cameroon . | 105°–125° | 126 | 157 | 68 |

The copals were extracted with ether and the solutions were shaken with 1 per cent. ammonium carbonate solution, which in neither case extracted anything ; 1 per cent. sodium carbonate solution extracted from the Angola copal two acids, angocopalolic acid ($C_{23}H_{36}O_3$, M.P. 85°, amorphous), and a resinous acid. The ether contained in solution an ethereal

oil, (B.P. 140°–160°, sp. gr. 0·853), and α-angocopalresene ($C_{30}H_{54}O_6$, or $C_{30}H_{56}O_6$, M.P. 63°–65°). From the portion of the resin insoluble in ether, a mixture of ether and alcohol extracted, along with some angocopalolic acid, yellow β-copalresene ($C_{25}H_{38}O_4$, M.P. 220°–224°). The insoluble portion resembled bassorin. The Cameroon copal was similarly treated, yielding cameroocopalolic acid ($C_{21}H_{36}O_3$, M.P. 98°–100°, amorphous), and a resinous acid; also a yellow essential oil (B.P. 145°–155°, sp. gr. 0·830), α-cameroocopalresene and β-cameroocopalresene ($C_{25}H_{36}O_4$, M.P. 220°–224°). There was also a residue, insoluble, resembling bassorin. The proportions are given below :—

| | Angola Copal. | | Cameroon Copal. |
|---|---|---|---|
| Angocopalolic acid . Resinous acid . . | 64 | Cameroocopalolic acid. Resinous acid . . | 70 |
| Essential oil . . . | 2 | Essential oil . . . | 2 |
| α-Angocopalresene . . | 3 | α-Cameroocopalresene . . | 3 |
| Acid soluble in ether alcohol | 5 | | |
| β-Angocopalresene . . | 20 | β-Cameroocopalresene . . | 20 |
| Bassorin (?) . . . | 0·3 | Bassorin (?) . . . | 3 |
| Ash . . . . . | 5·7 | Ash . . . . . | 2 |

**Zanzibar Copal.**—Tschirch and Stephan have examined Zanzibar copal by the usual method and have separated from it :—trachylolic acid ($C_{56}H_{88}O_8$, M.P. 165°), 80·0 per cent.; isotrachylolic acid ($C_{56}H_{88}O_8$, M.P. 160°), 4 per cent.; essential oil, etc., 9·46 per cent.; α- and β-copalresenes ($C_{41}H_{68}O_4$, and $C_{25}H_{38}O_4$), 6·00 per cent.; ash, 0·12 per cent.; impurities, 0·42 per cent.

W. Lippert and H. Reisseger somewhat modified the solvent in the determination of the acid and saponification values, using a mixture of alcohol and ether or chloroform and heating, then cooling before titrating for the acid value, but employing heat and alkali as usual for the saponification value. Their results are as follows. The resin was not completely soluble in all cases :—

| | Acid Value. | | Saponification Value. | Ester Value. |
|---|---|---|---|---|
| | Ether-alcohol. | $CHCl_3$-alcohol. | | |
| Angola, white | 59–61 | — | — | — |
| ,, red | 81–82 | 90 | 148–152 | 58–62 |
| Angostura | 28–35 | 48 | — | — |
| Benguela, selected | 61–62 | — | 111–126 | 50–64 |
| ,, ordinary | 84–87 | — | — | — |
| Brazil, selected | — | 153–158 | 148–157 | 1–5 |
| Cameroon | — | 106 | — | — |
| Kauri, selected | 81 | — | — | — |
| ,, clear, ordinary | 64 | 63 | — | — |
| ,, dark | 64·5–70 | 68–70 | 95–109 | 32–39 |
| Dammar | 33–35 | — | — | — |
| Madagascar | 25–30 | 60 | — | — |
| Manila, selected | 105–111 | 103–108 | 147–152 | 44–50 |
| ,, soluble in alcohol | — | — | — | — |
| Sierra Leone | 78–82 | — | — | — |
| Zanzibar | — | — | — | — |

## Manila Copal.

**Origin and Habitat.**—The product of *Agathis alba* (Lam.), *Dammara orientalis*. Philippine Islands. According to some writers it is derived from *Vateria Indica* (Dipterocarpaceæ).

**Chemical Constituents.**—Contains three resin acids, a volatile hydrocarbon, a neutral saponifiable substance, probably a lactone, and a resene. One of the acids, amounting to about 4 per cent. of the original resin, is crystalline, melts at 185°–187°, and has a composition represented by the formula $C_{10}H_{15}O_2$. The others are amorphous, and have the formulas $C_{22}H_{34}O_4$ and $C_{32}H_{50}O_4$. All three acids are monobasic. Over 80 per cent. of the resin is soluble in sodium carbonate solution (G. F. Richmond). According to Tschirch and Koch, the resin contains :—

| | I. Soft, dull sample. | II. Hard, lustrous sample from Celebes. |
|---|---|---|
| Mancopalinic acid . } Mancopalenic ,, . } | 4 | 0 |
| α-Mancopalolic acid . } β-Mancopalolic ,, . } | 75 | 80 |
| Mancopalresene . . . | 12 | 12 |
| Ethereal oil (sp. gr. 840, B.P. 165°–170°) } | 6 | 5 |
| Water . . . . . | 2 | 2 |
| Succinic acid and impurities . | 1 | 1 |
| | 100 | 100 |

**Appearance and General Characters.**—Occurs in large, irregular-shaped masses having a yellowish or brownish-yellow colour. Commences to melt at 105° C. and is completely fused at 140°. Specific gravity at 15° C., 1·069. Soluble in alcohol, also in mixtures of ethyl and amyl alcohols, and alcohol and ether. Only partially soluble in acetone, methyl alcohol, and acetone, and insoluble in turpentine (Bottler).

There are two kinds, hard, and friable.

H. Ingle has shown that Manila copal when finely ground and exposed to the light and air gained slightly in weight, while the iodine value decreased very considerably. He gives the following figures :—

| | Freshly ground. | After exposure for | | |
|---|---|---|---|---|
| | | 78 days. | 13 months. | 2 years. |
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| Iodine value . . . . | 134 | 106 | 94·5 | 88 |
| Acid value . . . . | 156 | 142 | 150 | 153 |
| Gain in weight . . . | — | 4·85 | 5·95 | — |

A. Rudling obtained the results given below :—

| | Water. | Substance Insoluble in Alcohol. | Acid Value. | Saponification Value | Iodine Value. |
|---|---|---|---|---|---|
| Manila (spirit soluble) | 2·10 | 2·30 | 136·6 | 187·6 | 106·0 |
| „ (hard) | 1·68 | 3·39 | 138·9 | 215·6 | 86·0 |

C. Coffignier has examined two samples of Manila copal and one of Pontianak copal, and gives the following particulars :—

| | Manila "Hard" Copal. | Manila "Friable" Copal. | Pontianak Copal. |
|---|---|---|---|
| Specific gravity at 17° | 1·065 | 1·060 | at 16° 1·037 |
| Softening point | 80° | 45° | 55° |
| Melting point | 190° | 120° | 135° |
| Acid number | 72·8 | 145·2 | 134·3 |
| Saponification number | 87·0 | 185·1 | 186·5 |
| Solubility in :— | | | |
| Ethyl alcohol | 44·10 | Soluble | Soluble |
| Methyl alcohol | 35·40 | 92·70 | 86·50 |
| Amyl alcohol | Soluble | Soluble | Soluble |
| Ether | 41·50 | 71·30 | 54·00 |
| Chloroform | 63·30 | 47·60 | 49·70 |
| Benzene | 36·10 | 42·10 | 37·00 |
| Acetone | 48·00 | Soluble | Soluble |
| Oil of turpentine | 26·80 | 35·90 | 33·60 |
| Benzaldehyde | 98·90 | 98·30 | Soluble |
| Aniline | Soluble | Soluble | Soluble |
| Amyl acetate | Soluble | Soluble | Soluble |
| Carbon tetrachloride | 31·00 | 38·00 | 38·10 |

Lippert and Reisseger found for the selected resin : acid value, 103–111; ester value, 44–50; saponification value, 147–152; and for samples soluble in alcohol, acid value 144–148. Williams gives acid value 131·6, ester value 52·5, saponification value 184·1, and iodine value 137·79; while Worstall, from analyses of 19 samples, gives the limits 104–148 for the iodine value.

**Resin from Dammara vitensis.**—A sample of this resin was shown in the Fiji Court at the Franco-British Exhibition in 1908, and was afterwards examined at the Imperial Institute. It consisted of a large mass, of a yellowish-brown colour, opaque, with translucent streaks, and containing particles of bark embedded in it.

It gave the following figures on examination :—

| | |
|---|---|
| Ash . . . . . | 0·06 per cent. |
| Melting point . . . . | 110°–115° |
| Acid value . . . . | 157 |

The resin dissolved completely in a mixture of alcohol and turpentine oil, was partly soluble in turpentine and in benzene, but almost insoluble in ether, chloroform, and alcohol. The resin is closely related to Manila copal from *Dammara orientalis*.

## Kauri.

**Origin and Habitat.**—Kauri is the product of *Dammara Australis* and is found in a fossil condition in the subsoil in the northern portion of the Auckland Provincial District of New Zealand. The resin is also sometimes found on living trees.

**Chemical Constituents.**—Tschirch and Niederstadt have examined kauri resin and have separated from it: kaurinic acid ($C_{10}H_{16}O_2$), 1·5; $\alpha$- and $\beta$-kaurolic acids ($C_{12}H_{20}O_2$, M.Pts. 81°–83° and 85°–87°), 48 to 50; kaurinolic acid ($C_{17}H_{34}O_2$, M.P. 128°–130°); and kauronolic acid ($C_{12}H_{24}O_2$, M.P. 86°–89°), 20–22; volatile oil (sp. gr. at 15°, 0·835; B.P. 156°–160°), 12·5; kauro resene (M.P. 63°-65°), 12·2, and bitter principle, 0·5–2·0 per cent.

**General Properties.**—Kauri occurs in angular or globular pieces which vary considerably in size from that of

a walnut to masses weighing sometimes as much as 100 lb. Colour, brown to dark brown or black. Occasionally transparent but more often translucent or opaque. Softens at 55°, melts at 150° C. and at 200° C. begins to decompose, yielding a distillate, the residual melted resin then being completely soluble in cold turpentine. Kauri dissolves almost entirely in a mixture of ethyl and amyl alcohols, it swells up in alcohol, and is partially soluble in ether, chloroform, acetone, methyl alcohol, and resin oils, but is insoluble in ordinary oils.

H. Ingle has shown that when kauri is finely powdered and exposed to air and light it increases in weight and the iodine value is lowered very considerably. He gives the following figures :—

| | Fresh. | After 78 days. | 13 months. | 2 years. |
|---|---|---|---|---|
| | Per cent. | Per cent. | Per cent. | Per cent. |
| Iodine value | 177 | 131 | 117 | 95 |
| Acid value | 51·7 | 59·5 | 69 | 74 |
| Gain in weight | — | 4·93 | 7·0 | — |

Coffignier gives the following solubilities, etc., for kauri :—

| | White Kauri. | Brown Kauri. | Bush Kauri. | Picked Bush Kauri. |
|---|---|---|---|---|
| Ethyl alcohol | 93·40 | 64·2 | 87·7 | 95·8 |
| Methyl alcohol | 50·4 | 38·1 | 52·7 | 65·8 |
| Amyl alcohol | Soluble | Soluble | Soluble | Soluble |
| Ether | 38·2 | 39·3 | 44·9 | 48·90 |
| Chloroform | 45·6 | 41·3 | 49·3 | 56·6 |
| Benzene | 33·3 | 29·1 | 38·3 | 42·4 |
| Acetone | 91·1 | 61·3 | 79·3 | 88·7 |
| Turpentine | 22·5 | 26·4 | 27·1 | 37·0 |
| Benzaldehyde | Soluble | Soluble | Soluble | Soluble |
| Aniline | Soluble | Soluble | Soluble | Soluble |
| Amyl acetate | Soluble | 98·0 | Soluble | Soluble |
| Carbon tetrachloride | 18·9 | 22·7 | 28·1 | 37·0 |
| Specific gravity | 1·036 | 1·053 | 1·03 | 1·038 |
| Melting point | 165° | 185° | 150° | 125° |
| Acid value | 70·9 | 78·8 | 83·1 | 81·8 |
| Saponification value | 73 | 89·7 | 78·5 | 87 |

Mills and Muter obtained for the kauri the figures :— saponification value 129, and bromine value 108·2.

Williams found the following :—

| | |
|---|---|
| Acid number | 52–63 |
| Ester number | 26–36 |
| Iodine number | 151–164 |
| Ash | 0·08–0·12 |

F. Ulzer and R. Defris found that by Twitchell's process, Angola copal and Kauri copal yielded respectively 86·01 and 86·37 per cent. of resin acids. Gladding's process was not applicable, since part of the soda soaps of the acids were precipitated from the alcoholic solution on addition of caustic soda, and a further separation took place on addition of ether.

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## 25. Dammar.

*Resina Dammar* (officinal in German Pharmacopœia III.).

**Origin and Habitat.**—Certain species of *Dammara* and *Hopea* (Burseraceæ and Dipterocarpeæ). Southern India.

**Chemical Constituents.**—Dammaroïc acid ($C_{54}H_{77}O_3(COOH)_2$), 23 per cent.; $\alpha$-dammar resene ($C_{11}H_{17}O$), 40 per cent. soluble in alcohol; $\beta$-dammar resene ($C_{31}H_{52}O$), 22·5 per cent. insoluble in alcohol, soluble in chloroform; ethereal oil and bitter principle, 0·5 per cent.; moisture, 2·5 per cent.; ash, 3·5 per cent.; impurities, 8 per cent. (Glimmann).

With regard to the "crystalline resinolic acids" recently isolated by Tschirch by fractional extraction, see *Ph. Ztg.*, 1899, No. 77.

**General Properties and Commercial Varieties.**—East Indian Sumatra dammar is in the form of stalactitic granules and lumps, yellowish, transparent, coated with dust, of vitreous conchoidal fracture, and harder than colophony. When chewed, dammar breaks down to a white powder, and it melts at 180° C. It is completely soluble in petroleum ether or chloroform, but only partially so in alcohol or ether. The intermediate resins between dammar and copal, such as Australian (or New Zealand) dammar = Kauri copal, are readily distinguishable (see below).

Among the dammars are grouped also—Saul resin, from *Shorea robusta* (Dipterocarpeæ, Sumatra and Java); Dammar Rata Kûtsching (Singapore), from *Hopea micrantha splendida*; and Dagieng, or Rose dammar (Borneo and Malacca), from *Retinodendron Rassak*; Selo-dammar (Singapore), from *Artocarpus integrifolia*; and "black dammar," of unknown origin (*Canarium strictum*, East Indies, and *C. rostratum*, Molucca Islands [?]). All these are rarely met with in European markets. Manila copal (*q.v.*), from *Vateria Indica*, is also called "white dammar."

The origin of the dammars has been dealt with by C. Müller in a valuable paper (*Ber. d. Deutsch. pharm. Ges.*, 1891, p. 365).

**Adulterants.**—Colophony, Australian dammar (Kauri copal).

**Analysis.**—As is well known, the generic term "dammar" includes a number of resins from trees of the families Dipterocarpeæ, Burseraceæ, and Coniferæ, as well as transitions into the copal group (such as Australian dammar, or Kauri).

For distinguishing copals from dammars, and the latter again from conifer resins—which also, to some extent, figure as "dammar" in commerce,—the Mauch chloral hydrate test may be recommended. True copals (*q.v.*) do not dissolve at all in 80 per cent. chloral hydrate solution, whereas true dammars, from *Dipterocarpeæ*, on the other hand, cede certain quantities to this solvent, the reaction being accompanied by a characteristic increase in volume; and conifer resins—like Kauri copal = West Indian dammar—are completely soluble. The solubility of the resins in epi- and di-chlorhydrin (Valenta) has already been referred to in Part I.; mention may also here be made of Hirschsohn's researches on twenty-three varieties, with the following results :—

| Dammar. | Solubility in— | |
|---|---|---|
| | Petroleum Ether. Per cent. | 85 per cent. Alcohol. Per cent. |
| East Indian | 88·03 | 87·97 |
| American | 83·42 | 83·90 |
| Dammar in massis | 77·18 | 77·60 |
| East Indian | 84·09 | 84·89 |
| D. viridis | 73·13 | 57·65 |
| Do. | 75·46 | 57·77 |
| D. nigra | 83·81 | — |
| D. marmorata | 54·12 | 53·98 |
| Do. | 30·20 | 29·99 |

The soluble constituents were dried at 120° C.

In utilising dammar for varnish-making, the resin is melted, like copal and amber, by which means it becomes soluble. A mixture of alcohol and oil of turpentine forms a good solvent. Weger (*l.c.*) has dealt with the absorption of oxygen by dammar when exposed to the air in thin layers.

Attention was bestowed on the examination of dammar by Brandes, Thomson, Dalk, Labillardiese, Giesecke, Müller, Mäusel, and others; and subsequent communications were made by Mills and Muter, von Schmidt, Erban, Kremel, Schweissinger, Williams, E. Dieterich, K. Dieterich, Gregor, Bamberger, and Mauch. (For the detection of colophony in dammar, by the Storch-Morawski reaction, see Colophony.)

Williams found—

| | |
|---|---|
| Ash | 0·01–0·07 per cent. |
| Loss on heating at 100° | 0·33–0·85 „ |
| Acid value (direct) | 21·00–26·00 |
| Saponification value (hot) | 21·0 –26·6 |
| Iodine value | 117·67–142·24 |

Von Schmidt and Erban have determined the solubility in various liquids as follows :—

| | |
|---|---|
| Alcohol | partial. |
| Ether | „ |
| Methyl alcohol | „ |
| Benzol | complete. |
| Petroleum ether | almost complete. |
| Acetone | partial. |
| Glacial acetic acid | „ |
| Chloroform | complete. |
| Carbon di-sulphide | „ |
| Oil of turpentine | „ |

Acid value (direct), 33·0; saponification number, 47·1; iodine value, 63·6.

E. Dieterich found 0·85 per cent. of moisture.

A. Kremel rightly confined himself to the direct acid value, in working with the usual method, and found—

| | Acid Value (direct). |
|---|---|
| Dammar | 31·0 |
| Do. | 34·3 |
| Do. (orient.) | 34·2 |

For "white dammar," which is identical with Manila copal (*q.v.*) from *Vateria Indica*, the same worker obtained the acid value, = 15·4. According to Mills and Muter, the saponification value of dammar is 52 and the bromine value 117·9.

E. Gottlieb has examined two samples of dammar from Central Borneo, the one being a recent dammar from *Vatica Rassak*, known as "dammar daging," the other a recent fossil resin. The results are given below :—

| | "Dammar daging." | Fossil dammar. |
|---|---|---|
| Melting-point | 130°–150° | 130°–150° |
| Acid value (direct) | 140–142 | — |
| ,, ,, (indirect) | 148·4–151·2 | — |
| Saponification value (cold) | 159·6–162·4 | — |
| ,, ,, (hot) | 163·5–165·2 | — |
| Resin acid soluble in | about | Resin acid soluble in |
| $Na_2CO_3(C_{24}H_{44}O_4)$ | 35 % | $(NH_4)_2CO_3(C_{16}H_{26}O_2)$ |
| Resin acid soluble in $KHO(C_{12}H_{26}O_3)$ | 30 % | $C_{11}H_{32}O_2$ |
| Essential oil | 15 % | $C_{12}H_{18}O_2$ |
| Resene ($C_{22}H_{28}O$) | 16 % | $C_{12}H_{22}O_2$ |

Several varieties of dammar have been examined by Coffignier, who gives the following results :—

| | Padang. | Borneo. | Singapore. | Pontianak. | Sumatra. | Batyan. |
|---|---|---|---|---|---|---|
| Specific gravity at 18° | 1·036 | 1·048 | 1·057 | 1·025 | 1·004 | 1·032 |
| Melting point . . | 95° | 120° | 95° | 110° | 190° | 105° |
| Acid value . . | 31·4 | 35·1 | 30·1 | 19·9 | 59·6 | 18·5 |
| Saponification value . | 33·7 | 64·5 | 39·3 | 30·9 | 64·5 | 19·6 |
| Percentage soluble in : | | | | | | |
| Ethyl alcohol . | 79·70 | 76·40 | 80·90 | 77·60 | 54·50 | 67·20 |
| Methyl alcohol . | 47·00 | 68·10 | 75·40 | 71·60 | 47·80 | 60·00 |
| Amyl alcohol . | 92·40 | 87·80 | 94·20 | 96·30 | 65·80 | 89·10 |
| Ether . . . | 95·50 | 90·40 | 99·00 | 95·90 | 62·10 | 96·80 |
| Chloroform . . | Soluble | 92·60 | Soluble | Soluble | 86·90 | 96·40 |
| Benzene . . | Soluble | 92·50 | Soluble | Soluble | 81·70 | 96·90 |
| Acetone . . | 85·30 | 79·60 | 86·00 | 83·60 | 54·70 | 78·70 |
| Spirit of turpentine | Soluble | 95·40 | Soluble | Soluble | 87·40 | 97·30 |
| Benzaldehyde . | Soluble | 92·00 | Soluble | Soluble | 75·30 | Soluble |
| Aniline. . . | Soluble | 84·00 | Soluble | Soluble | 67·20 | Soluble |
| Amyl acetate . | 93·80 | 89·90 | 95·90 | 95·40 | 70·00 | 92·70 |
| Carbon tetrachloride | Soluble | 91·60 | 97·50 | Soluble | 68·40 | 88·60 |

A sample of Batavia dammar was also soluble to the extent of 65·70 in methyl alcohol, 83·50 in acetone, and entirely soluble in aniline and benzaldehyde.

Nine different varieties of dammar resins from the Federated Malay States have been examined at the Imperial Institute. These were :—

1. Dammar Penak, No. 1 Quality from a species of *Balanocarpus*.
2. Dammar Kumus from a species of *Shorea* resembling *Shorea glauca*.
3. Dammar Mata Kuching from Port Dickson.
4. Dammar Soongyi.
5. Dammar Meranti from various species of *Shorea*. Inferior in quality.
6. Dammar Mata Kuching from Jempol.
7. Dammar Rengkong (?).
8. Dammar Merawan from a species of *Shorea*.
9. Dammar Strayah.

The results are tabulated below :—

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|---|---|---|---|---|---|---|---|---|---|
| Melting point . . | 90° | 94° | 87° | 180° | 185° | 92° | 200° | 97° | 190° |
| Ash, per cent. . . | 0·26 | 0·08 | 0·05 | 0·52 | 0·03 | 0·06 | 0·04 | 0·25 | 0·09 |
| Acid number . . | 45·3 | 72·0 | 38·5 | 33·0 | 72·0 | 33·0 | 46·5 | 38·5 | 55·0 |
| Ester number . . | 1·4 | — | — | 1·3 | — | — | 0·2 | — | — |
| Saponification number | 46·7 | 72·0 | 38·5 | 34·3 | 72·0 | 33·0 | 46·7 | 38·5 | 55·0 |
| Experts' classification | Clean, pale yellow | Black | Pale drop | Black | Chalky | Bold, pale | Green, like Ceylon | White | Chalky, inferior |

The following samples of dammar have also been examined at the Imperial Institute :—

| Derived from— | Black Dammar from Assam. | Rock Dammar from Burma. | |
|---|---|---|---|
| | *Canarium Bengalense.* | *Hopea Odorata.* | |
| | | I. | II. |
| Ash . . . . . | 0·78 | 0·55 | 0·68 |
| Melting point . . . . . | 125° | 115° | 90° |
| Acid number . . . . . | 8·15 | 31·5 | 31 |
| Ester number . . . . . | 1·28 | 5·6 | 0 |
| Saponification number . . . | 9·43 | 37·1 | 31 |
| Specific gravity . . . . . | — | — | 0·980–1·013 |

According to Glimmann, dammar is completely soluble in benzol, chloroform, and carbon di-sulphide ; and partially so in alcohol, toluol, acetone, aniline, petroleum ether, and acetic acid.

The researches of Graf, Tschirch, and Glimmann having shown that dammar is free from esters, the hot saponification and ester values determined by nearly all the above named workers—except K. Dieterich—have to be discarded. E. Dieterich very rightly concluded that, in view of the great fluctuations recorded in the ester value, it had better be left out of consideration.

The author has also shown that direct titration often gives unduly low acid values for dammar, because the resin

acid—especially in presence of the neutral constituents, and owing to the low acidity of dammarolic acid—does not always combine quantitatively. Hence, in the author's view, the values from direct titration are inferior to those furnished by the indirect method. The following modified method was therefore employed, which offers the additional advantage of dispensing with a preliminary process of solution :—

(*a*) *Acid value* (indirect).—One grm. of dammar is treated with 50 c.c. of benzine (sp. gr. 0·700), followed by 20 c.c. of alcoholic $\frac{n}{2}$ potash, the whole then being left for twenty-four hours, and afterwards titrated with $\frac{n}{2}$ sulphuric acid and phenolphthalein, without any addition of water. The acid value (indirect) is the product of the number of c.c.'s of KHO consumed, multiplied by 28·08.

(*b*) *Ash determination.*—Two grms. of the drug are carefully incinerated and calcined until constant, the weighings being made after cooling in a desiccator.

Formerly, the author employed alcoholic and aqueous alkali for the acid-value test, but found that the alcoholic solution alone is quite sufficient; and indeed, in the case of samples of dammar adulterated with colophony, it is particularly advisable to dispense with aqueous alkali, since the presence of water would lead to the decomposition of the colophony resin soap and furnish unreliable values. Consequently it is best to work with alcoholic alkali alone. The extreme limits of acid value obtained by the author with this method are 20–30; and the maximum permissible ash content is 0·1 per cent.

Dammar is often adulterated with colophony, for the detection of which Schweissinger recommended Kremel's acid value (direct) test. More recently the author has detected such adulteration by the abnormally high acid

values (indirect) obtained by the method described above; and has also shown that commercial dammar powder is impure, giving abnormally high acid values. Thus, dammar with 25 per cent. of colophony gave the acid value (indirect) 56·33–58·00, and with 50 per cent. 96·49–97·68, these results confirming the suitability of the method for this purpose. According to Hirschsohn, however, this method of detecting colophony is not reliable. The Hirschsohn test, which furnished good results in the hands of E. Dieterich, can also be recommended as a qualitative method for detecting colophony in dammar. The sample is treated with ammonia, and the liquid after filtration is supersaturated with acetic acid, whereupon, in the absence of colophony, the filtrate remains clear; but when colophony is present a precipitate is formed, the colophony being soluble in ammonia but thrown down in presence of acid. If the proportion of colophony be large, the entire acid liquid will become gelatinous.

For black dammar (probably from *Canarium rostratum*) and dammar from *C. strictum*, the following values have been obtained :—

| | Acid Value (indirect). |
|---|---|
| Black dammar . . . . . | 49·14–53·53 |
| Dammar from *C. strictum* . . . | 73·01–74·41 |

The author has recently found the acetyl values for dammar to be as follows :—

| | |
|---|---|
| Acetyl acid value . . . . | 50·52–51·80 |
| Do. ester value . . . . | 81·56–83·06 |
| Do. saponification value . . . | 132·08–134·86 |

Gregor and Bamberger obtained only negative results with the methoxyl value test.

(As to the utility of these values, and of the German Pharmacopœia tests, see references already cited under Colophony.)

For the determination of dammar in admixture with kauri, S. Stewart suggested a process in which the material is treated with absolute alcohol in a Soxhlett tube, the kauri being entirely soluble except for a small residue of vegetable fibre and mineral matter, while dammar yields about 36–48 per cent. insoluble in alcohol but soluble in chloroform. E. G. Parry, however, has shown that although the purer and finer grades of kauri behave towards alcohol as stated by Stewart, the darker and lower qualities are much less soluble. The following solubilities are given by Parry :—

| | Soluble in Absolute Alcohol. Per cent. | Soluble in Chloroform. Per cent. |
|---|---|---|
| Pure white kauri . . . . . | 89·9–94·3 | 40·8–47·2 |
| „ brown „ . . . . . | 61·9–74·2 | 38·7–42·3 |
| Pale " bush " kauri . . . . | 92·0–95·2 | 47·7–50·0 |
| Dark „ „ . . . . . | 79·5–84·0 | 41·9–45·0 |

H. Ingle proposed a similar method, the resin being first treated with a mixture of three parts of alcohol and one part of benzol, and the residue extracted with carbon bi-sulphide. Kauri and Manila copal yield no appreciable residue from the first-named mixture that is soluble in carbon bi-sulphide, whereas Herrol dammar left 36–44 per cent.

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## 26. Dragon's-Blood.

*Resina Draconis.*

**Origin and Habitat.**—I. Palm dragon's-blood, from *Dæmonorops Draco*, Bl. (Palmæ); II. Socotra dragon's-blood, from *Dracæna Cinnabari* (Dracænæ). South-eastern Asia, Socotra, West Indies, America.

**Chemical Constituents.**—I. Palm dragon's-blood. Draco-alban ($C_{20}H_{40}O_4$, M.P. about 200°), 2·5 per cent.; Dracoresene ($C_{20}H_{44}O_2$), 13·58 per cent.; benzoic draco-resinotannol ester ($C_6H_5COOC_8H_9O$); and benzoylacetic dracoresinotannol ester ($C_6H_5COCH_2COOC_8H_9O$)—forming together a pure red resin, or phenyl-$\beta$-monoxyacrylic draco-resinotannol ester (?)—56·86 per cent.; resin insoluble in ether, 0·33 per cent.; phlobaphene, 0·03 per cent.; vegetable residue, 18·40 per cent.; ash, 8·3 per cent. (Tschirch.)

Herberger found 90·7 per cent. of red resin which he termed draconin, 2·0 per cent. of fixed oil, 3·0 per cent. of benzoic acid, 1·6 per cent. of calcium oxalate, and 3·7 per cent. of calcium phosphate.

II. Socotra dragon's-blood.—Pure resin ($C_{18}H_{18}O_4$)—the author has recently found this to be a mixture of several resins, and not a definite chemical entity,—83·35 per cent.; gum, 0·7 per cent.; matter soluble in carbon di-sulphide, 0·48 per cent.; vegetable residue, 12 per cent.; mineral matter, 3·5 per cent. (Lojander.)

The following varieties contain benzoic acid, but no cinnamic acid :—Socotra, so-called " vera "; dragon's-blood, from *Dracæna Ombet Kotschy*; Socotra dragon's-blood, " sicut dicta," from *Dracæna Chizantha*, B.; and Palm dragon's-blood, from Banejrmasin (Borneo). The last-named contains draco-alban, whereas the others are deficient in this substance. (K. Dieterich.)

**General Properties and Commercial Varieties.**—Palm dragon's-blood (Sumatra) in bast is in the form of sticks, about eight inches long, and one-half to one inch thick, wrapped in Ligula leaves. Outside, it appears brown, but shows a red, lustrous fracture, and gives a light, red powder. On paper it leaves a red mark, and it is almost entirely soluble in alcohol and ether. The grade " in massa " is poor, and generally adulterated. Palm dragon's-blood alone answers to the author's " draco-alban " test, and is thus distinguishable from the Dracænæ varieties.

Socotra dragon's-blood occurs as irregular lumps of conchoid appearance, somewhat pitted, and of dark brownish red, lustrous colour. The fracture is pale, lustrous red, and the powder also light red. The substance is only partially soluble in alcohol and ether, and contains no draco-alban.

American (Mexican) and West Indian dragon's-blood, from *Pterocarpus* (*Croton*) *Draco*; dragon's-blood, from Venezuela and Columbia, and a few similar resins, are more nearly allied to Kino than to dragon's-blood, some are entirely obsolete. At present, Sumatra palm dragon's-blood is the only kind in commerce. A red resin resembling dragon's-blood is obtained from *Pterocarpus erinaceus* of Northern Nigeria.

**Adulterants.**—Ferric oxide, bole, artificial products made of resin, sandal-wood, gum, and colophony.

**Analysis.**—The commercial varieties of dragon's-blood are fewer than formerly, Sumatra palm dragon's-blood " in bast " and " in mass " being the principal kind. The technical application of this resin—for varnish in particular—is also very restricted. Analytical data are still very scanty, though adulterations with conifer resins and ferric oxide have been reported by several workers,—Bretet citing an

artificial product made of resin and powdered sandal-wood. Hirschsohn states that adulterated specimens are more soluble in petroleum ether than the pure drug.

Hilger and Wittstein report on adulterated products which can be distinguished at the first glance. Von Schmidt and Erban, and E. Dieterich, have estimated the iodine value, giving the figure 72·4. (For the detection of colophony by the Storch-Morawski reaction, see Colophony.)

Von Schmidt and Erban also found that dragon's-blood is only partially soluble in alcohol, ether, methyl alcohol, amyl alcohol, benzol, petroleum ether, acetone, glacial acetic acid, chloroform, carbon di-sulphide, and oil of turpentine; and the following degrees of solubility were determined by the author, for Sumatra dragon's-blood :—

| | |
|---|---|
| Alcohol<br>Ether | readily soluble. |
| Benzol<br>Chloroform<br>Acetic ether<br>Petroleum ether<br>Carbon di-sulphide | partially soluble. |

Von Schmidt and Erban characterised the solubility in ether and alcohol as partial, merely because the vegetable residue necessarily remained undissolved.

(On the solubility of dragon's-blood in epi- and di-chlorhydrin (Valenta), see Table in Part I.)

Williams found :—

| | |
|---|---|
| Acid value (direct) | 11·2 |
| Saponification value (hot) | 153·4 |
| Iodine value | 98·42 |
| Loss at 100° C. | 9·34 |
| Ash | 3·58 |

As, however, dragon's-blood contains no free acids, the acid values obtained are of merely relative worth. The Table drawn up by Hirschsohn for differentiating the various kinds of dragon's-blood is now no longer applicable.

Gregor and Bamberger determined the methoxyl value to be—

| I. | II. | III. |
|---|---|---|
| 27·6 | 25·3 | 33·8 |

Kitt obtained the carbonyl value 0·92.

The following acetyl acid values were found by the author :—Palm dragon's-blood, 139·07–139·79; but the corresponding ester and saponification values could not be determined, owing to the dark colour of the solution. (For the worth of these determinations, see *Chem. Rev.*, 1898, No. 10.)

The author examined a number of varieties of dragon's-blood by the fractional saponification method, the following procedure being adopted for determining the resin value and gum saponification value :—

(*a*) *Resin Value.*—One grm. of dragon's-blood is treated with 50 c.c. of ether and 25 c.c. of alcoholic $\frac{n}{2}$ potash, and left in a closed, glass-stoppered flask for twenty-four hours, the contents being then mixed with 250 c.c. of water and 100 c.c. of alcohol, and titrated with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The resin value is the product of the number of c.c.'s of KHO consumed, multiplied by 28·08.

(*b*) *Gum saponification value.*—One grm. of dragon's-blood is treated with 50 c.c. of ether and 25 c.c. of alcoholic $\frac{n}{2}$ potash, and left for twenty-four hours in a closed flask, at the end of which time it receives an addition of 25 c.c. of aqueous $\frac{n}{2}$ potash, and, after standing twenty-four hours longer, is titrated with $\frac{n}{2}$ sulphuric acid, in presence of phenolphthalein as indicator,—250 c.c. of water and 100 c.c. of

alcohol having been previously added. The volume of KHO consumed, multiplied by 28·08, gives the gum saponification value.

(c) *Draco-alban test.*—Ten grms. of powdered dragon's-blood are extracted with 50 c.c. of hot ether, the resulting solution being then concentrated to about 30 c.c. and poured into 50 c.c. of absolute alcohol. After leaving to settle for an hour, a white flocculent precipitate will be observed. (Characteristic for Palm dragon's-blood alone !)

The extreme limits of the above values determined by the author are as follows :—

| | | | |
|---|---|---|---|
| *A.* | Resin value . . . | 79·80–119·00 | Palm dragon's-blood. |
| | Gum saponification value . | 86·80–173·20 | |
| | Draco-alban test—positive. | | |
| *B.* | Resin value . . . | 81·20– 87·40 | Socotra dragon's-blood. |
| | Gum saponification value . | 92·40– 95·40 | |
| | Draco-alban test—negative. | | |

The draco-alban test was found to be characteristic of Palm dragon's-blood alone, and not for the varieties obtained from *Dracænæ*.

An addition of colophony—which seems to be a regular adulterant of the grades sold " in mass "—can be detected by the abnormally high resin value and gum saponification value ; and in such event Palm dragon's-blood answers very slowly to the draco-alban test.

According to Mauch, both Palm dragon's-blood and that from *Liliaceæ* are soluble in 80 per cent. chloral hydrate solution.

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## 27. Elemi.

*Resena Elema.*

**Origin.**—Various Burseraceæ, such as *Icica Icicariba*, *Amyris Plumieri*, and certain species of *Canarium*, like *C. commune*. According to Tschirch, Manila elemi is certainly derived from *C. commune*. The name elemi is generically applied to a large number of resins.

**Habitat.**—The Philippines, Central and South America, East and West Indies, Africa.

**Chemical Constituents.**—Manila elemi, or, as it is usually termed in commerce, "soft elemi," is the only kind that has been closely examined. It contains:—crystalline resin = amyrin ($C_{15}H_{42}O$), 25 per cent.; ethereal oil (dextrophellandrene, $C_{10}H_{16}$, and dipentene, $C_{10}H_{11}$), 10 per cent.; amorphous resin, 60–70 per cent.; small quantities of elemic acid ($C_{35}H_{46}O_4$), bryoïdin ($C_{20}H_{38}O_3$), and bitter principle (Flückiger). Amyrin, again, consists of two substances, with the formula $C_{30}H_{49}OH$ —*a*- and *β*-amyrin,—which are isomeric, and can be separated as acetyl derivatives, *α*-amyrin, M.P. 181°–181·5°, *β*-amyrin, M.P. 193°–194° (Vesterberg).

**General Properties and Commercial Varieties.**—In its fresh state elemi is a clear and light-coloured solution of resins in ethereal oil, with a portion of the resin crystallised out. Manila, or "soft," elemi is sometimes a viscid mass, rendered turbid by a crystalline deposit; at others, a soft, semi-crystalline, yellow resin; it may also be quite hard, and is then sold as "hard" elemi, the value of the material then being inferior to that of the soft variety. The smell of the fresh substance recalls lemons, fennel, mace, or good oil of turpentine.

American, or West Indian, Yucatan elemi generally forms "hard" commercial elemi. Formerly "soft" Yucatan

elemi was to be had, but this is now rarely the case.[1] Mexican, or Vera Cruz, elemi comes from *Amyris elemifera*, and is closely allied to Caranna resin (*q.v.*), from *Amyris Caranna*. Gum copal (or gum opal), from *Dacryodis hexandra* (a tree known in St. Lucia as "gomier à canots," on account of its resin being used for boats), is also a kind of elemi; and Cayenne incense, from *Icica heptaphylla*, is placed in the same class.

Brazilian Rio-elemi is a mixture of resins from species of *Protium*; also, according to Peckolt, one of the protium elemis is known in Brazil as "Almessega," and is probably derived from *Protium heptaphyllum*, M., var. *Brasiliense*, Engl. Brazilian elemi contains :—protomyrin, 30 per cent.; protolaminic acid, 25 per cent.; and protolaresene, 37·5 per cent. Protomyrin has the same formula and melting point as amyrin from the Manila variety.

In addition to the last-named resiniferous tree, *P. h.*, var. *venenosum* and *P. Brasiliense*, Engl., are also found in Brazil. Certain varieties similar to elemi are also known by the names—Resina tacamahaca, kikekunemalo, Resina caranna, Resina anime, the reason of this being that "elemi" is a generic term. East Indian elemi is said to come from *Canarium zephyrinum* (Moluccas).

African elemi (packed in bast like dragon's-blood) is derived from *Boswellia Freriana*, and is known as "Luban Matti"; it comes from Somaliland, via Cape Gardafui, and was formerly considered as a kind of incense (*q.v.*). Gomart gum from *Bursera gummifera* is a species of elemi, and has been recommended as a substitute for mastic (*q.v.*); this same gum is also classed along with incense (*q.v.*), the parent tree—also called "gommier"—being ranked with the so-

[1] As a rule, "soft elemi" is now understood to mean Manila elemi, and "hard elemi" that from Yucatan. This, though incorrect, is explainable by the fact that commercial Manila elemi is now generally soft, whilst Yucatan is nearly always hard.

called West Indian "incense trees." It should, however, be more properly relegated to the elemi group, in the same way as Occumé resin from West African (Gaboon) *Burseraceæ*. Numerous species of Icica furnish other varieties of elemi, now no longer met with in commerce. Resina Hedwigiæ [1] (*Hedwigiæ balsamifera*, Burseraceæ) and Resina Hyowæ are also counted as elemis, the second in particular being nearly allied to Caranna resin (see Flückiger's *Pharmacognosie*, p. 88). Other intermediate members between elemi and the incense group are not by any means rare (see under Incense, Caranna, Tacamahac, and Anime).

Apart from Manila and Yucatan elemi, all the known varieties are met with in the "hard" form exclusively.

The author has drawn up the following table of elemis, which, however, does not exhaust the list, though containing all the most important resins. (Tschirch groups the elemis with the resene resins—see Classification of Resins.)

### I. True Elemis—

| | |
|---|---|
| Soft and hard. | Manila elemi; from *Canarium commune;* generally met with in commerce in the "soft" state, but also sometimes as "hard." |
| | American or West Indian, Yucatan elemi; probably from *Amyris Plumieri;* usually "hard," formerly also met with in the "soft" form. |
| "Hard" only. | Mexican, or Vera Cruz elemi; probably from *Amaryis elemifera.* |
| | Rio elemi; probably a mixture of different Protium elemis. |
| | Brazilian Almessega elemi; probably from *Protium heptaphyllum*, M., var. *Brasiliense*, Engl. |
| | African elemi (Luban Matti); probably from *Boswellia Freriana.* |
| | East Indian elemi, probably from *Canarium zephyrinum.* |

[1] The balsam from *H. balsamifera*, the "baume à cochon" (hog balm), acts like copaiba (*q. v.*); its resin is the said Res. Hedwigiæ, and is classed by Hirschsohn as allied to elemi (see Table on next page).

### II. Varieties similar to Elemi—

(*a*) Those resembling elemi in odour, and most nearly allied thereto—

"Hard" only.
- East Indian Tacamahac; probably from *Calophyllum Inophyllum*.
- Bourbon Tacamahac; probably from *Calophyllum Tacamahaca*.
- Resina anime [1] from the East and West Indies; also derived from *Burseraceæ*.

(*b*) Those with an odour resembling incense, and more nearly allied to the latter.

"Hard" only.
- Cayenne incense; probably from *Icica heptaphylla*, etc.
- Gommart gum (also characterised as similar to mastic); from *Bursera gummifera*.
- Occumé resin; from a West African (Gaboon River) *Bursera*.
- West India Tacamahac; probably from *Icica heptaphylla*, etc.

### III. Varieties less closely approaching True Elemi in Odour and Appearance—

"Hard" only.
- Resina Caranna; probably from *Icica caranna*.
- Resina Kikekunemalo, Resina Hyowæ } from still unknown *Burseraceæ*.
- Resina Hedwigiæ; from *Hedwigia balsamifera*. (See footnote, p. 208.)
- Gum copal; Gommier resin from *Dacryodes hexandra*.

According to their colour, the author ranks Manila and Yucatan elemi among the white varieties; Resina anime and Vera Cruz elemi to the yellow to yellowish red kinds;

[1] For Anime, see also under Copal. Here, of course, the *Bursera* resin of elemi character is meant and not Courbaril, and the other soft copals usually termed "anime" in England. The identification of anime resin with Courbaril copal and the statement—frequently put forward in text-books—that *Hymenæa Courbaril* is the parent tree of anime resin is, of course, inaccurate.

whilst the African elemis, Protium elemis, and Tacamahacs, he groups with the grey to greyish black sorts with white-speckled surface of fracture. The more remote members—Res. caranna, Res. kikekunemalo, Res. Hyowæ, and Res. Hedwigiæ, etc., are dark-coloured to black.

The author has further observed that Resina Hyowæ is nearly allied to Caranna resin, and the latter to Vera Cruz elemi. Again, whilst West Indian Tacamahac is decidedly allied—already in the aroma—to incense, Bourbon and East Indian Tacamahac more resemble elemi.

Owing to the uncertainty of their origin, it is hardly possible to lay down any hard-and-fast limitation for the elemis, and more especially so because one and the same sort derived from the same kind of tree very often bears different names, according to where it has been gathered. So, for example, certain kinds of Tacamahac resin and cayenne incense are derived from *Icica heptaphylla*, notwithstanding their different names. Such a confusion of nomenclature cannot, of course, be cleared up except by a thorough study of the parent trees *in situ*—if this be possible. Although the foregoing list does not exhaust the elemi series—other intermediates to the incense species and other resins being known—the remainder are, however, too remote to deserve inclusion here. With regard to the identification of Bourbon Tacamahac with Caranna resin, and of West Indian anime with Tacamahac, see the summary of analytical data, and also under Caranna resin and Tacamahac.

**Adulterants.**—Other kinds of elemi.

**Analysis.**—The commercial varieties of elemi include not merely soft and hard true elemi, but also analogous resins (see above). As a rule, the only difference between the soft and hard varieties is in their content of ethereal oil, which latter imparts a balsamic consistency to the

"soft" kinds. Both varieties are largely used in varnish-making, to modify the consistency of the product. Hirschsohn proposed certain general colour reactions, which, however, were opposed by Buri as unreliable. The former worker also determined the solubility of a number of kinds in petroleum ether, and found it range from 30 to 90 per cent. (matter dried at 120° C.).

Von Schmidt and Erban found—

| | |
|---|---|
| Acid value (direct) | 22·3 |
| Ester value | 1·8 |
| Saponification value (hot) | 25·1 |
| Iodine value | 85·1 |

Solubility in—

| | | | |
|---|---|---|---|
| Alcohol | complete. | Petroleum ether | almost compl. |
| Ether | ,, | Acetone | complete. |
| Methyl alcohol | ,, | Glacial acetic acid | ,, |
| Amyl alcohol | ,, | Chloroform | ,, |
| Benzol | ,, | Carbon di-sulphide | ,, |
| | | Oil of turpentine | ,, |

A. Kremel found—

| | Manila Elemi. | Elemi. |
|---|---|---|
| Acid value (direct) | 3·0 | 17·5 |
| Ester value | 24·2 | 7·8 |
| Saponification value (hot) | 27·2 | 25·3 |

The figures obtained by Kremel for (presumably hard) elemi agree with those of von Schmidt and Erban and the author's (see below), who seem also to have had hard Yucatan elemi to work with.

On the other hand, the values given by E. Dieterich and Williams do not at all agree with the above, and they must either have dealt with adulterated products or else have used extracts in place of the natural drug. The values obtained by the author confirm those of von Schmidt, Erban, and Kremel, and are probably more near the truth.

Williams found—

| | |
|---|---|
| Acid value (direct) | 28·6 |
| Ester value | 129·0 |
| Saponification value (hot) | 157·6 |
| Iodine value | 175·39 |
| Ash | 0·04 per cent. |
| Loss at 100° | 3·50 „ |

No information is, however, given as to the kind of elemi examined.

E. Dieterich found, for soft elemi—

| | | |
|---|---|---|
| From extract. | Acid value (direct) | 26·30 |
| | Ester value | 103·60 |
| | Saponification value (hot) | 129·90 |

Solubility in—

| | | |
|---|---|---|
| Chloroform—almost complete | | |
| Oil of turpentine | 98·32 per cent. | soluble. |
| 90 per cent. alcohol | 98·26 „ | |
| Acetic ether | 97·79 „ | |
| Ether | 91·76 „ | |
| Benzol | 86·94 „ | |
| Carbon di-sulphide | 63·78 „ | |
| Petroleum ether | 44·86 „ | |

For estimating the acid value Kremel prepared a cold olution and titrated with $\frac{n}{2}$ alkali, Williams dissolved hot.

For the saponification value (hot) test, both authors employed heat under a reflux condenser for half an hour, and titrated the excess of alkali with $\frac{n}{2}$ sulphuric acid or $\frac{n}{2}$ hydrochloric acid. E. Dieterich saponified in the same way, but concentrated the liquid so as to expel the alcohol, and then redissolved the residue. He worked with an alcoholic extract. On the solubility of elemi in epi- and dichlorhydrin (Valenta)—see Table in Part I.

Mills and Muter found the saponification value 33 and the bromine value 122·2, and A Rudling gives the following figures:—

| | |
|---|---|
| Water | 0·2 |
| Insoluble in alcohol | 0·1 |
| Acid value | 22·4 |
| Saponification value | 28·0 |
| Iodine value | 83·6 |

Gregor and Bamberger found—

| | Gregor. | Bamberger. |
|---|---|---|
| Methoxyl value | 0·0 | 0·0 |
| | 2·5 | 0·0 |

(On the worth of these values, see *Chem Rev.*, 1898, No. 10.)

Recently, a large amount of analytical data referring to the various elemis has been contributed by the author, including the constants of several rare varieties.

From a number of preliminary experiments it became evident that, unlike many other resins, the elemis do not lend themselves to cold saponification, the values obtained by that method being always, although slightly, too low. The acid value was, therefore, determined by dissolving the sample in alcohol and titrating to redness in presence of phenolphthalein. The saponification value was ascertained by the hot method, the resin being boiled for half an hour with alcoholic $\frac{n}{2}$ potash; but in all cases the natural product in an unaltered condition was employed, and not in the state of an extract, the figures for the latter being of but little value.

It may be again mentioned that the author's values for Manila elemi agree very well with those of von Schmidt, Erban, and Kremel, but not with those of E. Dieterich and Williams, both of whom apparently employed extracts or adulterated samples, their values being tenfold those of the other workers. In other varieties of elemi no values are available for comparison.

With regard to the solubility tests and their results, detailed below, it should be noted that *two* results are in

many cases given, thus, for instance, "almost to completely soluble" indicating the difference in action of the same solvent when used "cold" and "warm." Where no difference was noticeable, only a single result is given.

The author has examined a large number of samples of elemi from various sources and obtained the following results :—

## I. Manila Elemi.

(*a*) *Soft.*

| | | |
|---|---|---|
| No. 1. | Loss at 100° C. . . . | 16·64 per cent. |
| | Ash . . . . . | 0·052 „ |
| | Acid value (direct) . . | 18·08 17·77 |
| | Ester value . . . | 7·64 9·91 |
| | Saponification value (hot) . | 25·72 27·68 |

Solubility in—

| | |
|---|---|
| Water . . . . | insoluble. |
| 96 per cent. alcohol . . | almost to completely sol. |
| Ether . . . . | completely soluble. |
| Acetic ether . . . | almost to completely sol. |
| Petroleum ether . . | sparingly soluble. |
| Benzine . . . . | partly to almost completely soluble. |
| Benzol . . . . | completely soluble. |
| Carbon di-sulphide . . | „ „ |
| Chloroform . . . | „ „ |
| Acetone . . . . | partly to completely sol. |
| Methyl alcohol . . . | sparingly to partly sol. |
| Amyl alcohol . . . | completely soluble. |
| Oil of turpentine . . | almost to completely sol. |
| Methylal . . . . | partly to completely sol. |
| Acetic anhydride . . | very slightly soluble. |
| Chloral hydrate (60 per cent.) | sparingly soluble. |
| Do. (80 „ ) | partly to completely sol. |
| Acetic acid . . . . | „ „ |
| Hydrochloric acid . . | sparingly sol. (rose red). |
| Sulphuric acid . . . | almost completely soluble (red-brown). |
| Ammonia . . . | insoluble. |
| Caustic potash . . . | insoluble. |

| | | | |
|---|---|---|---|
| No. 2. | Loss at 100° C. . . . | 11·71 per cent. | |
| | Ash . . . . . | 0·023 | ,, |
| | Acid value (direct) . . | 24·48 | 24·14 |
| | Ester value . . . | 25·45 | 25·84 |
| | Saponification value (hot) . | 49·93 | 49·98 |

Solubility, same as No. 1.

| | | | |
|---|---|---|---|
| No. 3. | Loss at 100° C. . . . | 17·71 per cent. | |
| | Ash . . . . . | 0·14 | ,, |
| | Acid value (direct) . . | 17·87 | 17·97 |
| | Ester value . . . | 8·11 | 7·72 |
| | Saponification value (hot) . | 25·92 | 25·69 |

Solubility, same as No. 1.

| | | | |
|---|---|---|---|
| No. 4. | Loss at 100° C. . . . | 15·14 per cent. | |
| | Ash . . . . . | 0·10 | ,, |
| | Acid value (direct) . . | 19·05 | 19·46 |
| | Ester value . . . | 6·15 | 6·03 |
| | Saponification value (hot) . | 25·20 | 25·49 |

Solubility, same as No. 1.

| | | | |
|---|---|---|---|
| No. 5. | Loss at 100° C. . . . | 19·29 per cent. | |
| | Ash . . . . . | 0·03 | ,, |
| | Acid value (direct) . . | 18·68 | 18·73 |
| | Ester value . . . | 6·70 | 7·71 |
| | Saponification value (hot) . | 25·38 | 26·44 |

Solubility, same as No. 1.

(*b*) *Hard.*

| | | | |
|---|---|---|---|
| No. 6. | Loss at 100° C. . . . | 8·46 per cent. | |
| | Ash . . . . . | 0·93 | ,, |
| | Acid value (direct) . . | 18·02 | 18·07 |
| | Ester value . . . | 26·99 | 24·40 |
| | Saponification value (hot) . | 45·01 | 42·47 |

Solubility in—

| | |
|---|---|
| Water | insoluble. |
| Alcohol (96 per cent.) | almost completely soluble. |
| Ether | partly soluble. |
| Acetic ether | almost to completely sol. |
| Petroleum ether | sparingly soluble. |
| Benzine | partly soluble. |
| Benzol | almost completely soluble. |
| Carbon di-sulphide | partly to almost completely soluble. |
| Chloroform | almost completely soluble. |
| Acetone | partly soluble. |
| Methyl alcohol | almost completely soluble. |
| Amyl alcohol | partly to almost completely soluble. |
| Oil of turpentine | partly soluble. |
| Acetic anhydride | ,, |
| Methylal | ,, |
| Chloral hydrate (60 per cent.) | ,, |
| Do. (80 ,, ) | ,, |
| Acetic acid | sparingly soluble. |
| Hydrochloric acid | insoluble. |
| Sulphuric acid | almost completely soluble (red-brown). |
| Ammonia | slightly soluble. |
| Caustic potash | ,, |

| | | | |
|---|---|---|---|
| No. 7. | Loss at 100° C. | 6·74 per cent. | |
| | Ash | 3·43 | ,, |
| | Acid value (direct) | 21·84 | 24·33 |
| | Ester value | 45·80 | 45·72 |
| | Saponification value (hot) | 67·64 | 70·05 |

Solubility, same as No. 6.

| | | | |
|---|---|---|---|
| No. 8. | Loss at 100° C. | 10·25 per cent. | |
| | Ash | 0·06 | ,, |
| | Acid value (direct) | 5·71 | 4·49 |
| | Ester value | 34·96 | 27·05 |
| | Saponification value (hot) | 40·67 | 31·54 |

Solubility, same as No. 6.

## II. Yucatan Elemi.

(*a*) *Soft.*

| | | | |
|---|---|---|---|
| No. 9. | Loss at 100° C. . . . | 17·07 per cent. | |
| | Ash . . . . . | 0·03 „ | |
| | Acid value (direct) . . | 22·50 | 22·29 |
| | Ester value . . . | 5·68 | 9·81 |
| | Saponification value (hot) . | 28·18 | 32·10 |

Solubility in—

| | |
|---|---|
| Water . . . . . | insoluble. |
| Alcohol (96 per cent.) . | almost completely soluble. |
| Ether . . . . . | „ „ |
| Acetic ether . . . | completely soluble. |
| Petroleum ether . . | slightly soluble. |
| Benzine . . . . . | slightly to almost completely soluble. |
| Benzol . . . . . | completely soluble. |
| Carbon di-sulphide . . | „ „ |
| Chloroform . . . . | „ „ |
| Acetone . . . . . | „ „ |
| Methyl alcohol . . . | partly to completely sol. |
| Amyl alcohol . . . | almost completely soluble. |
| Oil of turpentine . . | „ „ |
| Acetic anhydride . . | partly to completely sol. |
| Methylal . . . . . | almost completely soluble. |
| Chloral hydrate (60 per cent.) | imperfectly soluble. |
| Do. (80 „ ) | „ „ |
| Acetic acid . . . | partly soluble. |
| Hydrochloric acid . . | almost insoluble. |
| Sulphuric acid . . . | completely sol. (dark red). |
| Ammonia . . . | insoluble. |
| Caustic potash . . . | „ |

(*b*) *Hard.*

| | | | |
|---|---|---|---|
| No. 10. | Loss at 100° C. . . . | 17·86 per cent. | |
| | Ash . . . . . | 0·39 „ | |
| | Acid value (direct) . . | 1·16 | 1·70 |
| | Ester value . . . | 35·42 | 36·36 |
| | Saponification value (hot) . | 36·58 | 38·06 |

Solubility, same as No. 9.

## III. Vera Cruz Elemi.

| | | | | |
|---|---|---|---|---|
| No. 11. | Loss at 100° C. | 5·02 per cent. | | |
| | Ash | 0·24 „ | | |
| | Acid value (direct) | 5·98 | 5·64 | 11·72 |
| | Ester value | 40·29 | 28·34 | 37·32 |
| | Saponification value (hot) | 46·27 | 33·98 | 49·04 |

Solubility in—

| | |
|---|---|
| Water | insoluble. |
| Alcohol (96 per cent.) | partly to almost completely soluble. |
| Ether | completely soluble. |
| Acetic ether | partly to almost completely soluble. |
| Petroleum ether | insol. to very slightly sol. |
| Benzine | „ „ |
| Benzol | almost completely soluble. |
| Carbon di-sulphide | „ „ |
| Chloroform | „ „ |
| Acetone | partly to almost completely soluble. |
| Methyl alcohol | sparingly soluble. |
| Amyl alcohol | almost completely soluble. |
| Oil of turpentine | slightly to partly soluble. |
| Acetic anhydride | „ „ „ |
| Methylal | „ „ „ |
| Chloral hydrate (60 per cent.) | „ „ „ |
| Do. (80 „ ) | partly soluble. |
| Acetic acid | „ |
| Hydrochloric acid | almost insoluble. |
| Sulphuric acid | almost completely soluble. |
| Ammonia | slightly soluble. |
| Caustic potash | „ |

| | | | | |
|---|---|---|---|---|
| No. 12. | Loss at 100° C. | 4·90 per cent. | | |
| | Ash | 0·06 „ | | |
| | Acid value (direct) | 36·47 | 34·85 | 36·79 |
| | Ester value | 49·78 | 38·15 | 42·10 |
| | Saponification value (hot) | 86·25 | 73·00 | 78·89 |

Solubility, same as No. 11.

## IV. African Elemi (Luban Matti).

| | | |
|---|---|---|
| No. 13. | Loss at 100° C. | 6·06 per cent. |
| | Ash | 3·52 „ |
| | Acid value (direct) | 13·29 14·23 |
| | Ester value | 47·87 45·18 |
| | Saponification value (hot) | 61·16 59·41 |

Solubility in—

| | |
|---|---|
| Water | insoluble. |
| Alcohol (96 per cent.) | almost completely soluble. |
| Ether | „ „ |
| Acetic ether | slightly to almost completely soluble. |
| Petroleum ether | slightly soluble. |
| Benzine | „ |
| Benzol | almost completely soluble. |
| Carbon di-sulphide | partly to almost completely soluble. |
| Chloroform | almost completely soluble. |
| Acetone | slightly to partly soluble. |
| Methyl alcohol | slightly to partly soluble. |
| Amyl alcohol | partly soluble. |
| Oil of turpentine | almost completely soluble. |
| Acetic anhydride | partly to almost completely soluble. |
| Methylal | partly to almost completely soluble. |
| Chloral hydrate (60 per cent.) | slightly soluble. |
| Do. (80 „ ) | partly soluble. |
| Acetic acid | slightly soluble. |
| Hydrochloric acid | very slightly soluble. |
| Sulphuric acid | almost completely soluble. |
| Ammonia | slightly soluble. |
| Caustic potash | „ |

| | | |
|---|---|---|
| No. 14. | Loss at 100° C. | 1·86 per cent. |
| | Ash | 0·63 „ |
| | Acid value (direct) | 14·59 15·09 |
| | Ester value | 15·74 15·56 |
| | Saponification value (hot) | 30·33 30·65 |

Solubility, same as No. 13.

| | | | |
|---|---|---|---|
| No. 15. | Loss at 100° C. . . . | 5·89 per cent. | |
| | Ash . . . . . | 1·19 | „ |
| | Acid value (direct) . . | 35·80 | 37·33 |
| | Ester value . . . | 54·14 | 55·71 |
| | Saponification value (hot) . | 89·94 | 93·04 |

Solubility, same as No. 13.

## V. Indian Elemi.

| | | | |
|---|---|---|---|
| No. 16. | Loss at 100° C. . . | 3·38 per cent. | |
| | Ash . . . . . | 0·16 | „ |
| | Acid value (direct) . . | 32·46 | 35·77 |
| | Ester value . . . | 54·48 | 64·40 |
| | Saponification value (hot) . | 86·94 | 100·17 |

Owing to lack of material, the solubility could not be determined.

## VI. Protium (Allmessega) Elemi.

| | | | |
|---|---|---|---|
| No. 17. | Loss at 100° C. . . . | 2·87 % | 1·66 % |
| | Ash . . . . . | 0·32 % | 0·44 % |
| | In 96 per cent. alcohol . | insoluble | 3·65 % |
| | Acid value (direct) . . | 38·45 | 39·41 |
| | Ester value . . . | 35·82 | 34·23 |
| | Saponification value (hot) . | 74·27 | 73·64 |

Solubility in—

| | |
|---|---|
| Water . . . . | insoluble. |
| Alcohol (96 per cent.) . | almost to completely sol. |
| Ether . . . . | completely soluble. |
| Acetic ether . . . | partly to almost completely soluble. |
| Petroleum ether . . | slightly to partly soluble. |
| Benzine . . . . | very slightly soluble. |
| Benzol . . . . | almost completely soluble. |
| Carbon di-sulphide . . | „ „ |
| Chloroform . . . | completely soluble. |
| Acetone . . . . | partly to completely sol. |
| Methyl alcohol . . . | partly soluble. |

| | |
|---|---|
| Amyl alcohol | almost completely soluble. |
| Oil of turpentine | partly soluble. |
| Acetic anhydride | partly to almost completely soluble. |
| Methylal | slightly to partly soluble. |
| Chloral hydrate (60 per cent.) | partly soluble. |
| Do. (80 ,, ) | mostly soluble. |
| Acetic acid | partly to almost completely soluble. |
| Hydrochloric acid | almost insoluble. |
| Sulphuric acid | almost completely soluble. |
| Ammonia | slightly soluble. |
| Caustic potash | ,, |

## VII. Resina Gommart (Gommier Resin).

| | | | |
|---|---|---|---|
| No. 18. | Loss at 100° C. | 1·69 % | |
| | Ash | 0·14 % | 0·15 % |
| | Acid value (direct) | 46·41 | 47·42 |
| | Ester value | 53·76 | 51·92 |
| | Saponification value (hot) | 100·17 | 99·34 |

Two samples of Gommier resin from Dominica have been examined at the Imperial Institute, the results being as follows :—

| | Hard. | Soft. |
|---|---|---|
| Acid value | 14·1 | 37·3 |
| Ester value | 10·6 | 4·3 |
| Saponification value | 24·7 | 41·6 |
| Ash | 0·08% | 0·36% |
| Melting point | 158°–164° | below 100° |

## VIII. Anime.

| | | Acid Value (direct). | Ester Value. | Saponification Value (hot). |
|---|---|---|---|---|
| No. 19. | East India Anime | 29·69 | 29·77 | 59·46 |
| | | 30·64 | 38·67 | 69·31 |
| No. 20. | West India Anime | 45·36 | 113·93 | 159·29 |
| | | 47·20 | 102·39 | 149·59 |

## IX. Caranna Resin.

| No. 21— | I. | II. |
|---|---|---|
| Acid value (direct) . . . | 79·37 | 79·37 |
| Ester value . . . . | 110·48 | 111·84 |
| Saponification value (hot) . | 189·85 | 191·21 |

## X. Tacamahac Resins.

| | Acid Value (direct). | Ester Value. | Saponification Value (hot). |
|---|---|---|---|
| No. 22. Bourbon Tacamahac . | 38·10 | 68·22 | 106·32 |
| | 39·56 | 78·47 | 118·03 |
| No. 23. West Indian Tacamahac | 28·40 | 68·43 | 96·83 |
| | 22·71 | 75·88 | 98·59 |
| No. 24. Do. do. | 20·39 | 77·33 | 97·72 |
| | 27·75 | 95·15 | 122·90 |
| No. 25. East Indian do. | 32·99 | 38·81 | 71·80 |
| | 34·43 | 36·57 | 71·00 |
| No. 26. Do. do. | 21·41 | 32·67 | 58·04 |
| | 21·37 | 37·58 | 58·95 |
| No. 27. Do. do. | 22·20 | 60·90 | 83·10 |
| | 22·60 | 66·31 | 88·91 |

In conclusion, the following values were furnished by a Brazilian resin of the elemi type, known as "Almiscar," sent to the author by a friend:—

| | | | |
|---|---|---|---|
| Loss at 100° C. . . . . | 6·74 per cent. | | |
| Ash . . . . . | 0·54 ,, | | |
| Acid value (direct) . . . . | 25·35 | 22·48 | 26·39 |
| Ester value . . . . . | 51·38 | 30·51 | 36·45 |
| Saponification value (hot) . . . | 76·73 | 52·99 | 62·84 |

which results confirm the impression produced by the appearance and odour of the specimen, to the effect that it is allied to elemi.

From the foregoing series of results it is evident that the soft elemis differ, in the first place, from the hard kinds in their higher percentage of matter volatile at 100° C. In

certain cases the soft kinds also exhibit higher acid values, from which it may be concluded that the acid substances are present in the ethereal oil, or that the acids are dispersed or converted into anhydrides during the desiccation of the resins and their conversion into the hard form. These observations, however, could not be confirmed throughout. In all kinds the percentage of ash is very low, and the few instances where 3 per cent. and over was found were probably specimens contaminated by accidental mechanical impurities. One per cent. of ash is the highest permissible limit for good elemi. As regards solubility, all the varieties may be termed relatively easily soluble; ether being a particularly good solvent throughout, then alcohol, chloroform, carbon di-sulphide, benzol, and 80 per cent. chloral hydrate solution. Benzine and petroleum ether are the least effective solvents.

In respect of constants, the true elemis show comparatively low acid and saponification values; this applies to Manila elemi in particular. The scanty solubility of all elemis in ammonia and alkali is in itself an indication that no great amount of acid or ester-like constituents are present. The neutral "resenes" apparently predominate. This may also explain why elemi, being relatively resistant towards reagents, is largely used for softening varnishes. As a general rule the acid, ester, and saponification values seem to increase the more remote the specimen is from the *Καθ' ἑξοχήν* elemi—Manila elemi—on the list drawn up by the author and already detailed. This is seen most clearly in the case of Anime and Caranna resin, and still more so with Gommart. Protium (Almessega) elemi is more closely allied to the African and Indian kinds than to Manila elemi. The author was unable to confirm Hirschsohn's assumption that Bourbon Tacamahac is identical with Caranna resin (*q.v.*).

**Colophonia Elemi.**—A sample of Colophonia elemi from *Colophonia Mauritiana* has been examined by A. Tschirch and O. Saal. This sample came from Mauritius and had an acid value of 36 and a saponification value of 63. On treatment by the usual methods it yielded :—$\alpha$-isocolelemic acid ($C_{37}H_{56}O_4$, M.P. 120°–122°), 10 per cent.; coleleminic acid ($C_{39}H_{56}O_4$, M.P. 215°), 2 per cent.; $\beta$-isocolelemic acid ($C_{37}H_{56}O_4$, M.P. 120°), 8 per cent.; essential oil (B.P. 170°–175°), 3 per cent.; $\alpha$- and $\beta$-colamyrin ($C_{30}H_{50}O$), 25–30 per cent.; coleleresene ($C_{15}H_{24}O$, M.P. 75°–77°), 30–35 per cent.; bitter substance and bryodin traces, plant remains and impurities, about 10 per cent.

**Carana Elemi** from *Protium Carana* has also been examined by the same authors. The resin was collected in South-west Venezuela, and it yielded :—isocareleminic acid ($C_{40}H_{56}O_4$, M.P. 75°), 2 per cent.; careleminic acid ($C_{40}H_{56}O_4$, M.P. 215°), 8 per cent.; carelemic acid ($C_{37}H_{56}O_4$, M.P. 120°); essential oil (B.P. chiefly 170°–172°), 10 per cent.; $\alpha$- and $\beta$-caramyrin (M.Pts. 181° and 192° respectively), 20–25 per cent.; careleresene ($C_{27}H_{40}O_2$, M.P. 75°–77°), 30–35 per cent.; and impurities, 12–15 per cent.

**Caricari Elemi.**—A. Tschirch and L. Reutter have examined a sample of " caricari " resin which was exhibited at the Brazilian exhibition in Berlin in 1886. It had the acid number 27 and saponification number 59, and yielded :—isocarieleminic acid ($C_{38}H_{56}O_4$, M.P. 75°–76°), 5 per cent.; carieleminic acid ($C_{38}H_{56}O_4$, M.P. 215°), 12 per cent.; carielemic acid ($C_{37}H_{56}O_4$, M.P. 120°), 20 per cent.; essential oil, 20 per cent.; $\alpha$- and $\beta$-amyrin ($C_{30}H_{50}O$), 3 per cent.; carieleresene ($C_{24}H_{46}O_2$, M.P. 75°–76°), 40 per cent.; bitter substance, impurities, etc., 17 per cent.

The following are analyses of elemis from different localities examined at the laboratories of the Imperial Institute :—

| | Elemi from Southern Nigeria. | | Elemi from Liberia. | Uganda Elemi from *Canarium Schweinfurthii*. |
|---|---|---|---|---|
| | I. | II. | | |
| Ash, per cent. | 0·6 | 0·53 | — | 0·3 |
| Acid number | 65·3 | 37·8 | 22·6 | 29·4 (Picked sample) |
| Ester value | 6·6 | 8·4 | 22·1 | — (Picked sample) |
| Saponification number | 71·9 | 46·2 | 44·7 | 44·8 (Picked sample) |
| Volatile oil, per cent. | 8·1 | 4·4 | 9·5 | 11·2 |
| Solubility :— | | | | |
| Cold alcohol | Slight | Slight | — | Slight |
| Benzene | Complete | Complete | — | Complete |
| Turpentine | Nearly complete | Nearly complete | — | Slow and incomplete |
| Turpentine and alcohol | Complete | Complete | — | Complete |
| Characters of volatile oil :— | | | | |
| Colour | Pale straw yellow | Colourless or pale yellow | — | Pale straw yellow |
| Specific gravity at 15° | 0·8686 | 0·87–0·91 | 0·8679 | 0·8451 |
| Rotation in 100 mm. tube | + 50° 30′ Contains a large proportion of phellandrene | + 44° 3′ Contains phellandrene | dextro-rotatory | + 79° 20′ Contains much phellandrene |

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## 28. Guaiacum Resin.

*Resina Guajaci.*

**Origin and Habitat.**—*Guajacum officinale* (Zygophylleæ). Tropical America.

**Chemical Constituents.**—Guaiacum resin ($C_{20}H_{23}O_3$-OH); guaiaconic acid ($C_{20}H_{22}O_3(OH)_2$); guaiacic acid

($C_{21}H_{19}O_4(OH)_3$) (Hadelich's $\beta$-resin); guaiacol and guaiacum yellow ($C_{20}H_{20}O_7$). (Döbner and Lücker.)

According to Herzig and Schiff, guaiacum resin contains two HO groups, and two $OCH_3$ groups, whereas Döbner and Lücker found only one hydroxyl group. The difference in these results may be principally due to variation in the methods employed for acetylising.

**General Properties and Commercial Varieties.**—Guaiacum *in massa* forms a dark green to brownish black amorphous mass, dusty on the surface, of vitreous conchoidal fracture, transparent in thin splinters, and frequently contaminated with fragments of wood and bark. When chewed, the mass softens and has a strongly irritant taste. The resin melts at about 85° C., and resembles benzoin in odour. Its alcoholic solution is coloured a beautiful blue or green by oxidising agents. *Amber guaiacum* is merely a very pure kind of guaiacum, and has nothing in common with amber. The variety known as *alcohole depuratum* and *in lacrymis* is preferable to the *in massa* kind, on account of its greater purity, but is rarely met with in commerce.

**Adulterants.**—Colophony, and the very similar but yellowish brown resin, *Guajacum peruvianum odoriferum*.

**Analysis.**—Only two kinds of guaiacum are at present on the market in any quantity—the natural crude, and the purified resin; the variety "guaiacum in tears" is now very rare.

Ward found—

| | I. | II. | III. |
|---|---|---|---|
| Ash . . . . | 2·99 | 3·34 | 6·85 per cent. |
| Soluble in alcohol . . | 96·2 | 92·9 | 87·28 „ |
| Soluble in water . . | | 3·0–4·66 per cent. | |

According to Hager the points to be taken into consideration are—

Physical properties.
Solubility in chloroform and ethyl alcohol.

For the detection of colophony in guaiacum the same authority recommends the addition of an excess of caustic potash to the alcoholic solution, the colophony being thrown down as an insoluble rosin soap. The Storch-Morawski reaction for the same purpose has already been described under Colophony.

Hirschsohn found, for the solubility of this resin in petroleum spirit—

| | Soluble in Petroleum Ether— Dried at 17° C. | at 120° C. |
|---|---|---|
| Guaiacum *in granis* . . | 2·35 per cent. | 2·00 per cent. |
| Do. *lacrymis* . | 2·92 ,, | 2·01 ,, |
| Do. *massis* . . | 2·10 ,, | 1·80 ,, |
| Do. *do.* . . | 3·03 ,, | 2·40 ,, |
| Do. *do.* . . | 4·03 ,, | 3·97 ,, |

Kremel found—

| | I. | II. |
|---|---|---|
| Acid value . . . . | 23–28 | 44 |

and rightly limited his experiments to this value; Döbner and Lücker having, as already mentioned, found guaiacum to be free from ester, and to contain only resin acids similar to the phenols.

Evans' estimated the insoluble matter and ash, with the following results :—

| | Insoluble Matter. | Ash in Insoluble Matter. |
|---|---|---|
| Resin in blocks, *prima* . | 2·99 per cent. | 56·2 per cent. |
| Do. *do.* . | 7·66 ,, | 18·0 ,, |
| Do. *do.* . | 7·89 ,, | 23·1 ,, |
| Do. *do.* . | 10·00 ,, | 18·7 ,, |
| Resin in tears *do.* . | 1·54 ,, | 11·5 ,, |
| Do. *secunda* . | 9·00 ,, | 20·2 ,, |

Rabenau found—

| | I. | II. | III. |
|---|---|---|---|
| | % | % | % |
| Soluble in petroleum ether . | 0·06 | 0·02 | 0·01 |
| Soluble in ether . . . | 57·80 | 73·90 | 66·90 |
| Insoluble in ether and alcohol . | 9·90 | 6·10 | 12·20 |
| Ash . . . . . | 6·45 | 4·75 | 9·75 |

E. Dieterich found the following percentages soluble in—

| | *G. in massa.* | *Depuratum.* | *Naturale.* | *Pulveratum.* |
|---|---|---|---|---|
| 90 per cent. alcohol | 75·99 | complete. | 52·28–79·24 | 95·18 % |
| Acetic ether. . | 75·70 | ,, | 49·17–97·22 | 94·62 |
| Chloroform . . | 64·23 | ,, | 33·91–89·18 | 96·72 |
| Ether . . . | 69·91 | 90·66 | 22·93–80·56 | 87·08 |
| Benzol . . | 68·40 | 89·09 | 19·39–89·72 | 69·66 |
| Oil of turpentine . | 47·77 | 59·96 | 12·23–55·89 | 41·89 |
| Carbon di-sulphide | 27·81 | 34·33 | 12·41–23·69 | 34·46 |
| Petroleum spirit . | 6·69 | 6·16 | 1·93–10·06 | 6·31 |

The author has employed the following method for determining the acid value of guaiacum, and recommends reverse titration, in preference to the direct process, as a better means of securing a more suitable titration liquid and the complete combination of the resin acids.

(*a*) *Acid value* (indirect).—One grm. of resin is treated with 10 c.c. of alcoholic $\frac{n}{2}$, and 10 c.c. of aqueous $\frac{n}{2}$ caustic potash, and left for twenty-four hours in a flask fitted with a glass stopper. After adding 500 c.c. of water, the liquid is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein.

(*b*) *Ash.*—Two grms. of the drug are incinerated with care.

The values obtained were—

| | | | |
|---|---|---|---|
| G. *in massa*, acid value (indirect) | . | . | 89·60–92·50 |
| G. *depuratum* do. | do. | . | 89·60–97·50 |
| G. *in lacrymis* do. | do. | . | 72·00–75·60 |

The commercial grade " in massa " should contain not more than 10 per cent. of ash, whilst the " purified " and " in tears " kinds should contain much less than this. These last two kinds should be almost completely soluble in strong alcohol.

Adulteration with colophony is revealed by the very high acid values then furnished.

For detecting colophony and Peruvian guaiacum (*Guajacum peruvianum odoriferum*), Hirschsohn recommends bromine solution. The pure resin, dissolved in chloroform, should give with this reagent a blue coloration; adulterated specimens a red coloration. Petroleum ether will extract only 2–3 per cent. (see above) from the pure resin, but up to 42 per cent. from adulterated kinds. Also precipitating the alcoholic solution with water, and shaking the precipitate with caustic potash solution, when pure guaiacum dissolves to a clear liquid, but if colophony is present the liquid will be turbid. (According to E.Dieterich, the pure kinds yield over 3 per cent., some as much as 10 per cent., to this solvent.) According to Hirschsohn, if this solution is shaken with a 0·1 solution of cupric acetate, in presence of colophony the solution of the resin becomes blue or bluish green; with less than 10 per cent. of colophony it is necessary to concentrate by evaporation in order to detect the colour.

Mauch states that guaiacum is soluble in 60 per cent. and 80 per cent. solutions of chloral hydrate.

The author also determined the acetyl values, and found—

| | | Acetyl | |
|---|---|---|---|
| | Acid Value. | Ester Value. | Sapon. Value. |
| G. *depuratum* . | 13·57–14·89 | 149·33–149·75 | 163·22–164·22 |
| G. *in massa* . | 45·84–53·15 | 121·75–139·16 | 167·59–192·44 |

Gregor and Bamberger obtained the following methoxyl values—

| | I. | II. |
|---|---|---|
| Gregor, Methoxyl value . . . | 73·8 | 74·2 |
| Bamberger do. . . . | 83·8 | 84·0 |

From the above data, it is evident that the variety " in massa " is the poorest, and that " in tears " the best kind of guaiacum, the " purified " grade occupying an intermediate position. All three kinds are distinguishable by their acid value, ash content, and degree of solubility in alcohol.

Evans' obtained the following results in examination of commercial samples of guaiacum :—

| | |
|---|---|
| Acid value (indirect) . . . | 44·8–66·2 |
| Ash . . . . . | 1·5–11·7 per cent. |
| Inert matter . . . . . | 12·6–29·6 ,, |
| Soluble in petroleum ether . . | 0·5–2·6 ,, |
| Insoluble in 90 per cent. alcohol . | 20–32·3 ,, |

Portion soluble in alcohol :—

| | |
|---|---|
| Acid value . . . . . | 53·5–66·2 |
| Iodine value . . . . | 44–80·6 |

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**The Resins of Gutta-percha, Chicle and Balata.**—A sample of gutta-percha, from small plantations of Palaquium gutta grown in German New Guinea, yielded resins in which lupeol cinnamate predominated, but containing an

oily substance and a small proportion of a resene, so that the resins in this sample are different to those usually found in gutta-percha.

Gutta-percha consists, according to Payen, of three substances, the true gutta ($C_5H_8$), insomeric with india-rubber, and two resinous products, "albane" and "fluavile." Albane is a white crystalline substance soluble in hot alcohol, but not in cold; soluble also in benzene, carbon bisulphide, chloroform, and turpentine. According to Ramsey and others, it is soluble to the extent of 5·1 per cent. in cold and 54 parts in boiling alcohol, crystallising from the latter on cooling. It melts at 160° C. The composition of albane, according to Oudemans, is: carbon 78·91, hydrogen 10·44, and oxygen 10·65 (mean of two analyses), which corresponds closely with the formula $C_{10}H_{16}O$ ($C_{20}H_{32}O_2$). The melting point is stated by this observer to be 140° C. Oesterle gives the composition of albane as $C_{40}H_{64}O_2$, and its melting point as 165° C. According to Ramsey and others, however, albane is not a pure substance, but contains at least two compounds, one melting at 135°–160° C., having the composition $C_{16}H_{26}O$, and the other melting at 201°–204° C., having the composition $C_{17}H_{28}O$. Fluavile ($C_{40}H_{64}O_4$?) is a yellowish amorphous brittle resinous substance. It commences to soften at about 50° C., melts at 100°–110° C. (82°–85° C., Oesterle), and dissolves in cold alcohol, ether, benzene, carbon bisulphide, chloroform, and turpentine. According to analyses by Oudemans, fluavil contains: carbon 83·44, hydrogen 11·29, and oxygen 5·27 (mean of two analyses), which leads to the formula $C_{20}H_{32}O$. According to these analyses fluavil contains half as much oxygen as albane, and one might regard these substances as derived from the hydrocarbon $(C_5H_8)_4 = C_{20}H_{32}$ by simple addition in

the one case of one and in the other case of two atoms of oxygen.

Tschirch also describes other constituents of gutta-percha under the name of "albanans." These are insoluble in both hot and cold alcohol. The amount of total resins in gutta-percha varies very widely, according to E. F. A. Obach, from 11·2 to 67·4 per cent., while the figures given in Allen's *Organic Analysis* for the separate resins, according to various observers, are: alban 7·0 to 44·5 and fluavil 3·0 to 21·0 per cent.

**Gum Chicle.**—This is a product resembling gutta-percha in its properties, obtained from the latex of a Mexican tree, the *Achras sapota*. It is well known in the United States, where it is used almost entirely in the manufacture of "chewing-gum." A specimen of this product was examined by Tschirch and Schereschewski, who found it to contain 16·8 per cent. soluble in boiling water, 59·7 per cent. in boiling alcohol, 61·7 per cent. in boiling acetone, 76·2 per cent. in boiling ether, and 77·2 per cent. in chloroform. On adding alcohol to the aqueous extract about 9 per cent. of an optically inactive gum was obtained; this contained 3·76 per cent. of ash. The following substances were also separated and examined. They are soluble in alcohol in a similar manner to the resins of gutta-percha.

| | | Melting point. |
|---|---|---|
| α-Chiclalban . . | $C_{24}H_{40}O$ | 219°–222° |
| β-Chiclalban . . | $C_{18}H_{30}O$ or $C_{17}H_{28}O$ | 158°–159° |
| γ-Chiclalban . . | $C_{15}H_{28}O$ | 86°–87° |
| Chiclafluavil yield 1·5 per cent. . . | $C_{10}H_{18}O$ or $C_{10}H_{20}O$ | 66°–67° |
| Chiclalbanan . . | — | 55°–57° |
| and Chiclagutta . | $C_{10}H_{16}$ or $C_{10}H_{18}$ | Soluble in chloroform. |

The experiments of Tschirch and Schereschewski have

been repeated by Booz and Cohen, who come to the conclusion that the $\alpha$-chiclalban of the first-named observers is in reality nearly pure $\alpha$-amyrin acetate, that the $\beta$-chiclalban is a mixture of lupeol and $\alpha$- and $\beta$-amyrin in combination with caproic, acetic, and cinnamic acids; that $\gamma$-chiclalban is probably identical with cerotinone, and that chiclafluavil is a mixture made up of all the other constituents.

According to O. Sperber the tree from which gum Chicle is obtained (*Achras Sapota*) is indigenous to Mexico and Central America. It grows to a height of 40 to 50 ft., and with a trunk 35 to 40 in. in diameter. The wood of the tree is red, and may be mistaken for mahogany. The yield of gum is 30 to 35 lbs. per tree per annum. Tapping is resorted to at all periods except during the rainy season, V-shaped grooves being made through the bark. The latex as it issues is pale coloured, but it rapidly darkens on exposure to the air, and is subsequently heated to dry it and form it into a compact mass. The material is not imported directly into the United States as there is a high duty upon it, but is shipped to Canada, where it is further dried, losing about 50 per cent., and in this condition is exported to the United States. Some idea of the importance of this product may be arrived at by the fact that the imports into the States in 1909 amounted to 5,459,139 lb., valued at £417,000, with a yearly increase in the quantity. Experiments have been made with a view to the cultivation of the tree, 400 trees to the acre being planted; a calculation of the yield assumes that an eight to ten year old tree with a diameter of 12 to 15 in. will yield annually 5 to 6 lb. of the gum. In the manufacture of chewing-gum the material is kneaded with flavouring materials, such as vanilla, orange essence, etc., and sugar, and then moulded. On

chewing the product, the sugar and flavouring matters quickly dissolve out, leaving a soft doughy mass, similar to what one used to make at school by chewing wheat till the starch was removed, leaving gluten behind. Fortunately in this country there is not much demand for chewing-gum, although the American stuff is sold to a limited extent and sometimes also gluten; in the past, paraffin wax was used for the same purpose, but this was rightly condemned some years ago.

**Balata** is another product resembling gutta-percha, better known and of more importance from a commercial point of view, in this country, owing to the fact that it is used in the manufacture of belting for driving machinery.

Balata is the product of *Mimusops globosa* and comes into commerce in the form of thick sheets. This substance has also been examined by Tschirch and Schereschewski, who found it softened at 49°–50° C. to form a plastic mass, and became quite fluid at 149°–150° C. It was found to yield 5·7 per cent. soluble in boiling water, 41·5 per cent. in boiling alcohol, 42·5 per cent. in boiling acetone, 87 per cent. in boiling ether, and 86·8 per cent. in chloroform. The gum contained moisture 1·72 per cent., ash 0·96 per cent., resins (soluble in boiling alcohol) 41·5 per cent., and gutta (soluble in chloroform) 45·3 per cent. The product soluble in boiling water contained an albuminous substance precipitable by tannic acid, and a gum precipitated by alcohol, the yield of the latter being 1·5 per cent. of the weight of the balata, and the ash content 6·47 per cent. It was optically inactive, but gave the reactions of the carbohydrates including the pentosans (furfural-yielding substances). The alcoholic solution was found to contain two albans, the $\alpha$-balalban, $C_{27}H_{42}O_2$ melting at 230°–231° C., and the $\beta$-balalban $C_{27}H_{46}O_2$ melting at 108°–109° C., and a

fluavile, balafluavil $C_{10}H_{18}O$, the yield of which was small, *i. e.* $1\frac{1}{2}$ per cent.

The above resinous products did not contain the esters of cinnamic acid, but, as the authors point out, this does not distinguish them from the resins of gutta-percha, as the latter in some cases do, and in others do not, contain esters which yield cinnamic acid on heating with alcoholic potash. The chloroform solution contained the true gutta, balagutta $C_{10}H_{18}$, which rapidly alters on exposure to air, and also another substance—balalbanan $C_{20}H_{32}O_2$ or $C_{19}H_{32}O$, melting at 55° to 56° C.

**Phytosterols from Balata.**—The same author has also examined the $\alpha$- and $\beta$-balalban, which, according to Tschirch and Schereschewski, are constituents of balata. The $\alpha$-balalban was proved to be $\beta$-amyryl acetate. As lupeol is very often found in association with the amyrols, this was examined, and found to be present in the form of an ester, which was separated and purified by repeated crystallisation from alcohol. It forms white tablets melting at 208°–210°, and on saponification and crystallisation from alcohol, lupeol—melting point 210° C., crystallising in white needles—was obtained, while acetic acid was proved to be present in the liquid, so that the ester is a lupeol acetate. It is, however, not identical with lupeol acetate produced synthetically, as the latter melts at 215° C., and crystallises in needles. The author assumes from this that the lupeol in balata is not the ordinary lupeol, but is changed into that body on heating with alcoholic potash.

## 29. Jalapa Resin.

*Resina Jalapæ* (officinal in Germ. Pharm. III.).

**Origin and Habitat.**—*Ipomœa Purga*, Hayne (Convolvulaceæ). Mexico.

**Chemical Constituents.**—Convolvulin ($C_{31}H_{50}O_{16}$), insoluble in ether; also Jalapin = Orizabin ($C_{34}H_{56}O_{16}$), soluble in ether (W. Mayer). For a more extended examination of jalap resin see F. B. Power and H. Rogerson, *Pharm. Jour.*, 1909, p. 7.

**General Properties and Commercial Varieties.**—Long, round, dark, or black sticks, with lustrous fracture and dull exterior; practically insoluble in water, but soluble in alcohol and partly so in ether. According to Georgidas, *Convolvulus althœoides* also yields a resin, said to be suitable for replacing the officinal variety. It is contained, to the extent of 6–7 per cent., in the said *Convolvulacea* (Beyrout and vicinity), and contains 25 per cent. of substances soluble in ether.

**Adulterants.**—Resin from *Fungus Laricis*, colophony, guaiacum resin, aloes, myrrh, resin from Jalapa stalks, Tolu balsam.

**Analysis.**—A copious literature exists on Jalapa resin, especially with regard to the nodules from which the resin is artificially obtained by extraction with alcohol. Numerous workers have interested themselves with the percentage content of resin in Jalapa; and, as the question is an important one, their labours are recorded here.

Trommsdorf found 10·00–11·25 per cent. of resin; Dulk, 12·5 per cent.; Baudimont, 14 per cent.; Bernatzik, 9–12 per cent. Schwabe found at first 14 per cent.; later, only about 7 per cent. of resin, and was the first to confirm the retrogression of the Jalapa nodules in their resin content. Schacht found 10–12·5 per cent. of resin.

Guibourt found the following percentages of resin—

| I. | | II. | III. | |
|---|---|---|---|---|
| Officinal Jalapa— | | Orizaba Jalapa— | Finger Jalapa— | |
| Medium. | Young. | | Medium. | Young. |
| 17·65 | 14·68 | 8·00 | 7·38 | 3·91 |

It may be stated, therefore, that in general the younger nodules are poorer in resin than the older ones. Vulpius showed that they now contain not more than 10 per cent.; and Flückiger also confirmed the decrease to this figure, from the former rate of 20 per cent.

Von Ledden-Hulsebosch found that commercial Jalapa powder contains from 7–9·6 per cent., and states that 10 per cent. is scarcely ever attained at present.

E. Dieterich, in his pharmaceutical manual, gives the yield as 12–14 per cent. Bellingrodt placed it at 11·58 per cent., and later at 11·60 per cent., stating that 10 per cent. could well be regarded as a minimum. Waage found 12 per cent. of resin; Turner and Squibb, less than 10 per cent., viz. 7·32, 9·10, 8·72, 7·82, 6·51, 8·79, and 6·19 per cent. Alcock extracted with amyl alcohol, and also obtained below 10 per cent. Cripps found over 10 per cent. in fourteen kinds, and more than 12 per cent. in seven; he gave the lowest limit as 5 per cent. and the highest 15 per cent.

That the percentage of resin in Jalapa nodules has decreased in the course of years, and that inferior goods are in the market may therefore be regarded as proved. This remark, unfortunately, applies to almost all natural drugs. Perhaps this is due to an inferior method of collection, or maybe to some fermentation process which did not occur formerly. For it has been shown by E. Dieterich that, whereas an unfermented gentian root yields 40 per cent. of extract, fermented root yields only 20 per cent. Such fermentation might occur through the careless piling up of large quantities of the drug.

Bearing the first-named point in mind, the German Pharmacopœia, No. II, was a little too modest in fixing the minimum amount at as low as 7 per cent. of resin, against which clause both Thoms and Bellingrodt rightly raised

objection, desiring to fix 10 per cent. as the minimum; indeed, in view of the fact that other Pharmacopœias demand 10 and even 12 per cent., the aforesaid minimum of 7 per cent. seems to be decidedly too low. The author approves the 10 per cent. proposed by Thoms, since, if traders find the Pharmacopœia so complacent, they are likely to still further lower the standard of their wares, in the expectation that the limits prescribed by the Pharmacopœia will be again reduced.

So far as the examination of Jalapa is concerned, the expensive nature of the drug has caused this to be widely advocated and attempted.

Colophony, extracts, and false Jalapa resins are the main adulterants. Laneau describes an adulterated resin which yielded 90 per cent. to ether, whereas only 2 per cent. is soluble in the case of the pure resin. For the Storch-Morawski reaction for colophony, see the description of that resin. Bernatzik, in his comprehensive treatise on Jalapa, gave a method for detecting false resin, based on the divergent solubility of the two resins in chloroform. According to G. Weigel, the solubility in chloroform is much greater than 10 per cent., as given in some Pharmacopœias, and he proposes to use ether in place of it, in which not more than 10 per cent. is soluble, whereas scammony dissolves to the extent of 80 per cent. or more. Kohlmann, however, characterised the method as tedious, and proposed instead that the specific gravity should be used as a distinctive indication, that of the pure resin being 1·146, and of stalk resin, 1·047; and on the basis of this difference he calculated the percentage of both in a mixture. This method seems to the author to be rather untrustworthy, since it is clear that the pure resin, containing as it does more or less air, cannot have a constant specific gravity.

How much the more then is the quantitative calculation a risky procedure! The author's experience shows that the method requires to be employed with circumspection. (Compare the specific gravity found by Beckurts and Brüche, given below.)

The former Pharmacopœia Committee advised the ammonia test as a characteristic one, the resin being warmed with ammonia—whereby the convolvulin is converted into convolvulinic acid—and the filtrate treated with an acid, whereupon any colophony present is liberated as a flocculent or gelatinous precipitate, the convolvulinic acid not being precipitated from the ammoniacal solution. Later, however, the committee, having found that nearly all Jalapa resins, even when pure, give a precipitate with acid, modified the method so that 2 grms. of resin warmed with 10 grms. of ammonia should furnish a solution that would not gelatinise. The German Pharmacopœia, No. III., prescribes non-gelatinisation with ammonia, and mere turbidity with acetic acid. This latter test is, however, not to be relied on, as there are few if any resins that will give nothing more than turbidity with acid, most of them yielding a precipitate. Further on it is required that the resin shall produce no coloration when ground in a tenfold quantity of water. Unfortunately the ammonia test in its original form has found its way even into the most recent textbooks, whereas only the modified form, without addition of acid, is acceptable. Hirsch, in his critique on the American Pharmacopœia, states that the resin left after evaporating the ethereal solution of the drug and redissolving in 5 per cent. caustic potash is precipitated by acid, whereas the portion insoluble in ether does not yield a precipitate when treated in the same manner.

In any case, no great reliability can be placed on these

qualitative tests, which is corroborated by the fact that later investigators occupied themselves with quantitative examinations on the usual analytical lines, leaving these particular tests in the background.

We are indebted, for the first quantitative values, to Kremel, who found—

| | Acid. Value (direct). | Ester Value. | Saponification Value (hot). |
|---|---|---|---|
| Jalapin . . . . | 14·7 | 172·9 | 187·6 |
| Jalapa resin . . . | 12·9 | 119·8 | 132·7 |
| Do. . . . | 12·1 | 120·7 | 132·8 |

Kremel stated that the one sample of Jalapa resin was prepared by himself, the other being a commercial product. Concordance in the values furnished by two resins of entirely different origin indicates that the method employed is the correct one. An addition of colophony would give a considerably augmented acid value.

On the basis of an examination of a considerable number of specimens, Beckurts and Brüche formed the conclusion that the specific gravity, solubility in alcohol, and the acid, ester, and saponification values are suitable for determining the purity of Jalapa resin, and for the detection of adulteration. Unfortunately they do not appear to have subjected any adulterated specimens to examination in this manner: at least they do not refer to any in their communication.

They found—

| | Sp. gr. | Acid Value (direct). | Ester Value. | Saponification Value (hot). |
|---|---|---|---|---|
| 1. | 1·143 | 15·0 | 110 | 125 |
| 2. | 1·147 | 13·0 | 121 | 134 |
| 3. | 1·150 | 18·0 | 111 | 129 |
| 4. | 1·151 | 27·0 | 109 | 136 |
| 5. | 1·149 | 11·0 | 118 | 129 |
| 6. | 1·149 | 20·0 | 113 | 133 |
| 7. | 1·149 | 14·0 | 126 | 140 |

The percentage soluble in (alcohol free) chloroform should not exceed 6, as was also laid down by Hager.

The above values agree well with those of Kremel, thus showing that the acid and saponification values are distinctly useful in testing Jalapa resin.

According to the *Chemist and Druggist*, Sage examined nodules that had been stored for twenty-eight years, but found them little richer in active constituents than freshly collected specimens. He obtained 11·34 per cent. of total resin, only 7·5 per cent. of which was soluble in ether (0·85 per cent. soluble, and 10·49 per cent. insoluble in ether).

In a number of samples of the jalap root examined by Evans', the amount of resin extracted by 96 per cent. alcohol amounted to 5–16 per cent. on the natural root or 7–18·7 per cent. on the dry powder. The small tubers gave the lowest yield, *i. e.* 5–7·5 per cent. They give the following analyses of resins extracted by them :—

| | Yield of Resin from Moist Tuber. | Acid Value. | Ester Value. | Saponification Value. | Iodine Value. |
|---|---|---|---|---|---|
| 1. | 5 per cent. . . | 25·1 | 128·4 | 153·5 | 18·4 |
| 2. | 7 ,, . . | — | — | 168·8 | 15·6 |
| 3. | 11 ,, . . | 26 | 142 | 168 | 24·2 |
| 4. | 12·5 ,, . . | 23 | 162 | 185 | 13 |
| 5. | 15 ,, . . | 13·8 | 141·2 | 155 | 23 |
| 6. | 16 ,, . . | 8·4 | 144·9 | 153·3 | 11·2 |
| | Ether insoluble, 92·4 per cent. | 9·3 | 147·7 | 157 | 5·4 |
| | Ether soluble . | — | — | — | 100 |
| 7. | 21 per cent.. . | 23 | 121·8 | 144·8 | 9 |

W. B. Cowrie gives the methods of testing jalap resin, and states that commercial " white jalap resin " contains 3–3·1 per cent. of moisture, ·02–·022 per cent. of ash, 0·3 per cent. soluble in ether. The acid value was 2·8, the saponification value 417, and the optical rotation $[a]_D = -37·5°$. Two samples of brown jalap resin gave :—moisture, 5·0–5·6

per cent.; ash, 0·3 per cent.; soluble in ether, 10 per cent.; acid value, 11·2–14 per cent.; saponification value, 333–338 per cent. Jalapin, the resin of jalap which is insoluble in ether, had the acid value 2·8; saponification value, 408; and optical rotation, $[a]_D = -39·5°$.

Hooper attributes the variations in the resin content of the nodules to be due to the character of the soil, and especially to the influence of phosphates.

The author has reported on the quantitative examination of pure Jalapa resins prepared by himself, and also of adulterated specimens, as well as on the interesting results obtained by W. Hampe in the Helfenberg laboratory, showing the influence exercised by additions of colophony, guaiacum, and gallipot on the normal values given by Jalapa resin.

The method adopted was as follows :—

(*a*) *Acid value* (direct).—One half-grm. of *Resina Jalapæ* is dissolved in 50 c.c. of ethyl alcohol and titrated with alcoholic $\frac{n}{2}$ potash and phenolphthalein, preferably in a tall measuring cylinder.

(*b*) *Saponification value* (hot).—One half-grm. is dissolved in 50 c.c. of alcohol, treated with 25 c.c. of alcoholic $\frac{n}{2}$ caustic potash, and heated for an hour on the steam bath. After cooling in a loosely closed vessel, the liquid is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The number of c.c. of alcoholic potash consumed per 1 grm. of resin, multiplied by 28·08, gives the saponification value.

This is the same method Kremel employed with which he obtained the lower values already cited.

The same method applied to two resins prepared by the author from *Tubera Jalapæ* gave very concordant results—

| | I. Res. Jal. | II. Res. Jal. | Referred to dry substance. I. Res. Jal. with 3·4 % loss on drying. | II. Res. Jal. with 4·96 % loss on drying. |
|---|---|---|---|---|
| Acid value (direct) | 26·58 | 27·30 | 27·52 | 28·72 |
| | 27·13 | 27·30 | 28·09 | 28·72 |
| Sapon. val., (hot) | 244·72 | 234·04 | 253·32 | 246·30 |
| | — | 234·04 | — | 246·30 |

Since these figures do not agree with those of the authors quoted above, further experience is necessary to decide which are the more correct. Those now given should be correct, seeing that they were obtained with perfectly pure resins prepared at first-hand.

In order to determine the value of the method for detecting adulteration, it was applied to purposely adulterated Jalapa resins. Three of the most customary adulterants were added, in the proportions of 10 and 20 per cent., to the sample II. Res. Jalapæ. The effect of these additions is seen in the following analyses :—

| | Resina Jalapæ ipse parat. | The same with— 10 % Colophony. | 20 % Colophony. | 10 % Guaiacum. | 20 % Guaiacum. | 10 % Gallipot. | 20 % Gallipot. |
|---|---|---|---|---|---|---|---|
| Acid value (direct) | 27·30 | 39·08 | 54·07 | 32·13 | 39·62 | 42·29 | 56·75 |
| | 27·30 | 39·08 | 53·54 | 29·45 | 39·08 | 41·76 | 56·21 |
| Saponification value (hot) | 234·04 | 231·84 | 221·76 | 221·76 | 202·16 | 221·76 | 211·12 |
| | 234·04 | 231·84 | 223·44 | 221·20 | 204·96 | 221·76 | 211·12 |

Thus colophony, even in small amount, largely increases the acid value; Resina guaiaci considerably depresses the saponification value; and gallipot, like colophony, raises the acid value. The influences exercised by even small proportions of these adulterants would be appreciable.

The same mixtures were examined by the test prescribed by the Germ. Pharm. III., with the result that no objection would be taken, on the basis of this test, to those which contained 10 per cent. of any of the adulterants, or even that

containing 20 per cent. of guaiacum. The defect of this method lies in the fact that the added resins are soluble in ammonia, and that a portion of the Jalapa resin is also precipitated from the ammoniacal solution.

The following results were obtained in the examination of a commercial specimen of Jalapa resin which had been purposely adulterated with powdered gum and also with colophony :—

| | Resina Jalapæ pulv. adulterated with | | |
|---|---|---|---|
| | Gum. | Gum and 25 % of Colophony. | Gum and 50 % of Colophony. |
| Acid value (direct) | 18·82 | 53·15 | 97·27 |
| | 19·37 | 53·70 | 97·27 |
| Sapon. val. (hot) | 154·50 | 164·60 | 180·30 |
| | 155·20 | 164·60 | — |

These figures show that the method is very well adapted for the detection of adulterants, an assumption which agrees with the experience of the authors already cited.

The carbonyl value has been determined by Kitt, who found it = 1·02.

Gregor and Bamberger applied the methoxyl value test with negative results.

(For the value of these determinations, see *Chem. Rev.*, 1898, No. 10.)

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## 31. Labdanum.

*Resina Ladanum seu. Labdanum.*

**Origin and Habitat.**—*Cistus Cypricus, C. Creticus, C. ladaniferus* (Cistineæ). Cyprus, Crete, and Southern Europe generally.

**Chemical Constituents.** — According to Guibourt, Cyprus labdanum *in massa* contains resin, 86 per cent.; ethereal oil, 7 per cent.; wax, earthy matters, and impurities, such as hair, 6 per cent.; extractives, 1 per cent. Resin and volatile oil 86, watery extractive 7, insoluble 8 (Holmes). The so-called labdanum *in tortis* (twist) contains 20 per cent. of resin, 1·9 per cent. of wax, 0·6 per cent. of malic acid, 3·6 per cent. of gum; ferruginous sand, ethereal oil (together 73·9 per cent.). Sand 72, resin 20, gum and malate of lime 6, wax 1·9 (Pelletier). Volatile oil 2·9, resin 53·9, ash 23·6 (E. Weiss).

E. J. Emmanuel separated from Cretan ladanum, by treatment of the ethereal solution with $Na_2CO_3$ solution, a resin acid which was brown and viscid. The residue, insoluble in ether but soluble in alcohol, formed a viscid, clear brown resin. On distillation with steam the residue from the ethereal solution yielded an essential oil having a specific gravity of 0·928, B.P. 225°, and a refractive index at 15° of 1·5118, and on heating at a higher temperature a solid, colourless crystalline substance—ladaniol ($C_{17}H_{30}O$, M.P. 89°)—passed over. This was similar to champacol and guaiol, described by Wallach and Tuttle (*J. Chem. Soc.*, A, 1894, i. 538). The residue of ladanum, insoluble both in ether and in alcohol, contained a bassorin-like gum yielding mucic acid when heated with nitric acid, a greyish-white resene, and a bitter principle.

**General Properties and Commercial Varieties.**—Whereas, formerly, labdanum was largely used and highly esteemed as an agreeably scented resin rich in ethereal oil, the only kind now in the market is "Ladanum usu Candia," a Cretan product, which is very impure and for the most part artificial. At one time a very quaint method was employed for collecting this resin, by driving flocks of sheep through the *Cistus* shrubs, and gathering the resin that adhered to the wool. The hairs found by Guibourt (see above) had their origin in the resin in this manner. The grades in the French and German markets are very divergent in character, which implies that the perfectly pure article has vanished and been replaced by artificial products.

Labdanum is in the form of dark brown or black, viscid masses, which soften in the fingers, and exhibit a grey fracture when freshly broken, but soon turning black. It is insoluble in water, but almost completely soluble in alcohol. The odour, especially of the ethereal oil, is agreeable, like ambergris; the flavour balsamic and biting. The solubility in ether is 61 per cent., chloroform 69, alcohol 57 per cent. Practically insoluble in water and light petroleum. Ash 12 per cent. (E. J. Emmanuel).

Labdanum in rods, such as was formerly met with in commerce, seems to have been a very impure kind derived from *Cistus ladaniferus*.

**Adulterants.**—Artificial products made from colophony, sand, and plumbago. Labdanum was formerly used to adulterate storax.

**Analysis.**—As already mentioned, labdanum at present enjoys only a very limited application, so that its analysis is relatively unimportant. Nevertheless, the values obtained by the author from different kinds, of French and

German origin, may be recorded here, it being remarked that they refer to present day commercial varieties, and that no data on pure labdanum from earlier times are in existence. Hirschsohn, also, regarded as artificial the kinds examined by him in 1877.

The author found—

| | Acid Value (direct). | Ester Value. | Sapon. Value (hot.) |
|---|---|---|---|
| 1. Lad. veritable (French commercial grade) | 90·37 | 116·10 | 206·47 |
| | 91·98 | 120·26 | 212·24 |
| 2. Do. do. | 98·05 | 102·06 | 200·11 |
| | 98·36 | 109·88 | 208·24 |
| 3. Res. Lad. vera (German commercial grade) | 54·08 | 167·87 | 221·95 |
| | 54·69 | 161·95 | 216·64 |
| 4. Do. do. | 54·01 | 166·88 | 220·89 |
| | 51·85 | 168·39 | 220·24 |
| 5. Ladanum usu Candia | 113·81 | 87·88 | 201·69 |
| | 114·80 | 87·98 | 202·78 |
| 6. Ladanum in pani (loaves) | 14·06 | 47·64 | 61·70 |
| | 13·42 | 39·46 | 52·88 |

Whereas the French and German grades show a moderate degree of concordance, especially in the saponification value figures, No. 6 sample was a very impure specimen, and the values accordingly come out very low. In general, as already stated, the existing commercial grades of labdanum seem to be artificial products or mixtures.

Gregor and Bamberger found the methoxyl value = 0. (For the worth of these values, see *Chem. Rev.*, 1898, No. 10.)

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## 32. Mastic.

*Mastix.*

**Origin and Habitat.**—*Pistacia lentiscus* (Anacardiaceæ). Mediterranean littoral; cultivated in Chios.

**Chemical Constituents.**—Dextro-rotatory ethereal oil ($C_{10}H_{16}$), 2 per cent. (Flückiger). Also various resins, particularly: $\alpha$-resin ($C_{40}H_{64}O_4$), mastic acid (soluble in alcohol), and $\beta$-resin = masticin ($C_{40}H_{64}O$) (Johnston), and bitter principle.

A. Tschirch and L. Reutter found a specimen of mastic from Chios to have an acid number of 59, saponification number 82·5. By the usual method of treatment they separated from it: $\alpha$- and $\beta$-masticic acids ($C_{23}H_{36}O_4$, melting respectively at 90°–91° and 89·5°–90·54°), 4 per cent.; masticolic acid ($C_{23}H_{36}O_4$, M.P. 201°), 0·5 per cent.; $\alpha$-masticonic acid ($C_{32}H_{48}O_4$, M.P. 96°–96·5°), 20 per cent.; $\beta$-masticonic acid ($C_{32}H_{48}O_4$, M.P. 91°–92°), 18 per cent.; $\alpha$-masticoresene ($C_{35}H_{56}O_4$, M.P. 74°–75°), 30 per cent.; $\beta$-masticoresene, 20 per cent.; essential oil, 2 per cent.; bitter substance, impurities, etc., 5·5 per cent.

The volatile oil, according to Schimmel, amounts to 0·9–2·5 per cent., and has a strong balsamic odour resembling that of the resin; it has a specific gravity of 0·855–0·87 at 15°, and the optical rotation in 100 m.m. tube + 22° to + 27°.

**General Properties and Commercial Varieties.**—Levantine mastic, the ordinary commercial variety, is in the form of rounded, pale yellow granules (tears) which are hard, with conchoidal fracture, which soften when chewed (in which latter respect it differs from sandarach); sp. gr. 1·074; it is almost entirely soluble in alcohol (a

portion, however, only swells in this liquid, and to this Hlasiwitz gives the formula $C_{20}H_{30}O$), ether, chloroform, benzol, carbon di-sulphide, and ethereal oils; but the greater part is insoluble in petroleum ether. *Pistacia terebinthina* yields a balsam resembling mastic, known as "Chios turpentine" (see Turpentine).

Indian Bombay mastic—which is little dealt in—comes from Central Asiatic species of *Pistacia* (*P. Cabulica* and *P. Khinjak*). A substitute for mastic is found in "Gommart gum," from *Bursera gummifera*, which should more properly be classed with the elemis (*q.v.*). The name "Gommart" is derived from "Gommier" (gum tree) applied to this species of *Bursera*, which is also termed "birch tree" in Jamaica, and belongs to the so-called "incense trees" (see Incense).

"American mastic," formerly so styled, comes from *Schinus molle*, a Mexican plant belonging to the *Anacardiacea* (see Hartwich, *die neuen Arzneidrogen*, p. 303).

**Adulterants.**—Sandarach, colophony (especially in powder), *Resina pini*, sea salt.

**Analysis.**—Mastic being readily confounded with sandarach, it is advisable, before proceeding further, to note their points of difference, which will again be dealt with fully under Sandarach. This last-named has a higher acid value and breaks when chewed, whereas mastic softens. Furthermore, mastic is the more soluble in benzol, and in 60 per cent. chloral hydrate solution (in which sandarach is practically insoluble); both are soluble in 80 per cent. chloral hydrate. In oil of turpentine, mastic is readily and almost completely soluble, whereas sandarach is only partly soluble, and that, too, with difficulty. For the degree of solubility in epi- and dichlorhydrin, see Valenta's Table in Part I.

The following values relate to ordinary commercial Levantine varieties (Williams) :—

| | I. | II. |
|---|---|---|
| Acid value (direct) | 50·40 | 56·00 |
| Ester value | 23·00 | 23·10 |
| Saponification value (hot) | 73·40 | 79·10 |
| Iodine value | 158·62 | 159·00 |
| Ash | 0·21 % | 0·14 % |
| Loss at 100° | 0·97 % | 1·46 % |

The acid, ester, and saponification values were determined by the usual method. These values, however, should not be regarded as final, since, according to the present state of our knowledge of the chemical composition of mastic, the ester-like constituents appear to be absent.

The solubility according to Hirschsohn is as follows :—

| | Soluble in Petroleum Ether of— | | |
|---|---|---|---|
| | B.P. 40° C. | 60° C. | 80° C. |
| Mastic | 50·96 % | 71·56 % | 75·86 % |
| Do. | 51·89 % | — | — |
| Do. | 38·49 % | — | — |
| Bombay mastic | 12·50 % | — | 12·45 % |

Kremel found—

| | I. | II. |
|---|---|---|
| Acid value (direct) | 61·8 | 70·9 |

by dissolving the substance in ether alcohol, and redissolving in water as soon as precipitation commenced. The ether and saponification values were not determined.

Von Schmidt and Erban obtained the following results :—

| | |
|---|---|
| Acid value (direct) | 64·0 |
| Ester value | 29·0 |
| Saponification value (hot) | 93·0 |

Solubility in :—

| | |
|---|---|
| Alcohol | partial. |
| Ether | complete. |
| Methyl alcohol | partial. |
| Amyl alcohol | complete. |
| Benzol | ,, |
| Petroleum ether | insoluble. |
| Acetone | partial. |
| Glacial acetic acid | ,, |
| Chloroform | ,, |
| Carbon di-sulphide | slight. |
| Oil of turpentine | partial. |

C. Coffignier has also determined the solubility of mastic and found:—87·50 per cent. soluble in methyl alcohol, 90·70 in acetone, 93·90 in aniline, and completely soluble in benzaldehyde.

Mills and Muter found the saponification value 117 and the bromine value 124·3.

Some kinds appear to be almost entirely insoluble in petroleum ether, whilst others are partially soluble therein.

E. Dieterich found the acid value (direct) to be 67·2 by the same method as Kremel.

The author has found that reverse titration furnishes more concordant results than the direct method, in the case of mastic, and that, moreover, the colour-change from red to yellow is more sharply defined than the converse change in the direct method; the (indirect) titration method also dispenses with the necessity for previously dissolving the substance. For the reason already given, no attempt was made to determine the ester and saponification values. The method adopted is as follows :—

One grm. of mastic is treated with 50 c.c. of benzine (sp. gr. 0·700) and 20 c.c. of alcoholic $\frac{n}{2}$ potash, and left for twenty-four hours in a tightly closed glass-stoppered flask,

the contents being then titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein, without any addition of water.

The values obtained were :—

| | Acid Value (indirect). | | | |
|---|---|---|---|---|
| | I. | II. | III. | IV. |
| Mastic electa . | 44·80 | 46·20 | 44·80 | 47·60 |
| Mastic electa pulv. . | 107·80 | 109·20 | 110·60 | 113·40 |
| Mastic naturale . | 51·80 | 53·20 | 53·20 | 53·20 |
| Do. . | 65·28 | 65·99 | — | — |
| Mastic, Bombay . | 109·20 | 109·20 | 103·89 | 103·89 |
| Do. . | 137·60 | 139·89 | — | — |
| Mastic, Turkish . | 90·56 | 90·26 | — | — |

The figures agree very well, and show, in the first place, that Indian (Bombay) mastic is distinguishable from ordinary Levantine mastic by its higher acid value, and also that the " pulvis " variety is apparently adulterated (probably with colophony) like nearly all commercial powdered resins (see remarks at end of Part I.). The acid values found by the chemists already named also correspond fairly well with the author's figures. Direct titration furnished somewhat lower values. Preliminary experiments showed that while both aqueous and alcoholic alkali may be used with about the same results with pure samples, alcoholic alkali alone is more practical and advisable for the detection of any added colophony, the addition of water during titration being also preferably avoided. Tested in the above manner, the Levantine (ordinary commercial) mastics give acid values between 40 and 70, the Bombay kinds 100–140, whilst the Turkish variety yields figures midway between the two. The U.S. Pharmacopœia fixes the acid value at not less than 65.

Gregor determined the methoxyl value of mastic, and found from 0–1·9.

According to Mauch, mastic is partly soluble in both

60 per cent. and 80 per cent. chloral hydrate solutions (see above, distinction from Sandarach). For the Storch-Morawski reaction for detecting colophony, see Colophony.

**Resin from Pistacia terebinthus, var., Palästino.**—Louis Reutter has examined an aromatic resin from this source. It had a melting point of 70°–71°, acid number 126·16–130·54, saponification number 235·87–241·14, and ester number 106·7–110·6. The resin contained abundant needle-shaped crystals and gave the reactions for cholesterol. On distillation in a current of steam it yielded a volatile oil, of sp. gr. 0·8516, refractive index 1·4622, and optical rotation $(a)_D - 17° 18'$, from which borneol separated on standing. From the resin were isolated the following constituents: Pistacic acid ($C_{18}H_{26}O_3$), amorphous, M.P. 104°; pistacolic acid ($C_{24}H_{42}O_3$), colourless and crystalline, M.P. 148°–148·5°; $\beta$-pistacolic acid ($C_{21}H_{34}O_3$), white powder, M.P. 148°–149·5°, acid number 101·08–101·12; $\alpha$-pistacolic acid ($C_{19}H_{30}O_3$), white powder, M.P. 91·5°–92·4°, acid number 61·77–62·15; pistacinolic acid ($C_{22}H_{38}O_2$), yellowish-white crystals, M.P. 138°; $\alpha$-pistacinolic acid ($C_{18}H_{30}O_2$), white powder, M.P. 103°–104°; $\alpha$-terpentinic acid ($C_{26}H_{44}O_3$), large colourless crystals, M.P. 110°–111°; $\beta$-terpentinic acid ($C_{21}H_{26}O_3$), white powder, M.P. 82·5°–84°, acid number 78·6–78·89; also $\alpha$-pistaciresene ($C_{29}H_{48}O_3$), amorphous, M.P. 96°–97·5°, and terpentinoresene, amorphous, M.P. 79°–81°.

## Morhal Resin.

D. Hooper has examined a sample of resin from *Vatica lanceæfolia* (Blume) which inhabits Eastern Himalaya, Assam, Eastern Bengal, and Burma, and is known by the natives as "morhal." It is a pale brown brittle resin, dissolving completely in turpentine. It dissolves to the

extent of 48 per cent. in alcohol, while 84 per cent. is soluble in ether. The acid value of the product was 15·4 and the iodine value 69·3.

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## 33. Resina Pini.

*Pine Resin.*

**Origin and Habitat.**—Various species of *Pinus: P. Pinaster, P. picea, P. sylvestris, Larix Europæa.* Europe.

**Chemical Constituents.**—True pine resin contains oil of turpentine, dextro-pimaric acid (M.P. 211° C.), and lævo-pimaric acid (M.P. 150° C.), $C_{20}H_{30}O_2$, which crystallise well.

Tschirch recently succeeded in isolating new " crystallisable resinol acids " (see under Turpentine, and also *Ph. Ztg.*, 1899, No. 77) by fractional separation from pure resins of *Pinus picea, P. sylvestris*, and several other species of *Pinus.* In contrast to colophony " Resina Pini " contains esters.

*Gallipot* is a variety of pine resin, poor in oil, containing pimaric acid, but only a very little ethereal oil.

*Gum Thus* or *American Frankincense* contains from 4–8 per cent. of essential oil and is soluble in an equal volume of 90 per cent. alcohol.

*Barras* contains a considerable amount of impurities, in addition to the above constituents.

The *Resina Pini raffinata* used in pharmacy (*Terebinthina cocta*) is not the same as the above pine resin, since it is a

residue from the distillation of turpentine, and contains water. It differs from colophony in that—like the hydrated "*Aloe hepatica*"—it is crystalline and hydrated, instead of anhydrous and amorphous. Anhydrides are found only as traces, if any, the bulk consisting of hydrates of abietic and allied acids, ethereal oil being practically non-existent in this variety.

The exudation resin from *Pinus Laricio* has been subjected to a close chemical examination by Bamberger and Landsiedl. They found the following to be present:—

$\alpha$-Resin, which is a mixture of abietic pinoresinol ester, with a smaller proportion of paracumaric pinoresinol ester; also pinoresinol, $C_{17}H_{12}O_2(OH)_2(OCH_3)_2$, and $\beta$-resin, which is an ester of pinoresinotannol, $C_{30}H_{28}O_4(OCH_3)_2(OH)_3$.

The exudation resin from *Larix decidua* (larch) has also been examined, and found to contain—

Abietic acid and lariciresinol, $C_{14}H_{10}(OCH_3)_2(OH)_3$ (Bamberger and Landsiedl). These authors have more recently determined the formula of lariciresinol to be $C_{17}H_{12}(OCH_3)_2$-$(OH)_4$, two of the four free HO groups being phenolic, the others alcoholic in character. On boiling lariciresinol with acetyl chloride, a tetracetyl derivative, $C_{17}H_{12}(OCH_3)_2$-$(OCH_3CO)_4$, melting at 160° C., was obtained; the action of acetic anhydride on potassium lariciresinol, however, furnished the triacetyl product, $C_{17}H_{12}(OCH_3)_2(OCH_3CO)_3$, M.P. 92° C. Two other derivatives of lariciresinol were also prepared, namely, the di-methyl ether, $C_{17}H_{12}(OCH_3)_4$-$(OH)_2$, and the di-ethyl ether, $C_{17}H_{12}(OCH_3)_2(OC_2H_5)_2(OH)_2$.

**General Properties and Commercial Varieties.**—Whereas the resins known as "Resina Pini" are hard, the ordinary turpentines (*q.v.*), also obtained from species of pine, are of soft, balsamic consistence, though more nearly allied to the resins than to the balsams.

Natural pine resin is a sticky, yellowish mass, smelling of turpentine, and mixed with impurities.

**Gallipot.**—*Resina Pini raffinata* (*Terebinthina cocta*), *Resina alba*, *Pix alba*, and Burgundy pitch are opaque, crystalline masses, containing little or no ethereal oil, and of variable colour and water content. Both the last-named properties are dependent on the duration of exposure to heat, and on the melting temperature. *Barras* is only externally impure; otherwise it resembles natural pine resin.

The exudations at the margin between the blaze and the bark in black fir are covered with a peculiar resin to which the term exudation resin has been applied (see above), and which, though merely of theoretical interest, is worthy of mention.

The ordinary pitch, the boiled and hardened turpentine-free conifer resin, is met with in commerce as yellow, or white, Burgundy pitch, shoemakers' wax, and brewers' pitch; the last-named variety melting readily to a thin fluid. Mannite pitch is a very impure form of brewers' pitch.

**Analysis.**—J. Brand states that brewers' pitch is generally loaded (up to 13·12 per cent.) with mineral matters. The so-called mannite pitch is a kind which contains up to 32·12 per cent. of ferruginous compounds (iron glance), and is therefore unsuitable for brewers' use.

**Adulterants.**—Vegetable and mineral impurities, artificial products from colophony, oil of turpentine, and oil of wormwood.

**Analysis.**—In view of the divergent names applied to pine resins, especially gallipot, *Resina Pini*, *Resina Pini raffinata* and *depurata*, and also of the fact that, in many countries, *Resina Pini raffinata* and different intermediate kinds of pine resin are called gallipot, it is not surprising that the analytical data show only a relative degree of con-

cordance. In addition it is to be remarked that the percentage of ethereal oil plays a conspicuous part in influencing the values, just as with the gum resins. Whereas colophony contains no esters, these substances are present in all varieties of *Resina Pini*, and hence the existing ester and saponification values must be regarded as justified.

The acid values determined by A. Kremel are as follows :—

| | Acid Value (direct). |
|---|---|
| I. Resina Pini | 77·8 |
| II. Resina Pini depurata | 102·6 |
| III. Pix burgundica | 142·2 |

He did not, however, determine the ester and saponification values.

Mills and Muter found for gum thus :—

| | |
|---|---|
| Saponification value | 210 |
| Bromine value | 108·5 |

Evans' gives for Burgundy pitch :—

| | |
|---|---|
| Acid value | 126–164·5 |
| Saponification value (hot) | 134·4–172·9 |

E. Dieterich found—

| | |
|---|---|
| Acid value (direct) | 145·44–161·16 |
| Ester value | 9·95– 28·66 |
| Saponification value (hot) | 157·16–188·96 |
| Loss at 100° C. | 12·50 per cent. |
| Ash | 1·0 ,, |

Solubility in—

| | |
|---|---|
| Alcohol (90 per cent.) | complete. |
| Chloroform | ,, |
| Acetic ether | ,, |
| Benzol | ,, |
| Carbon di-sulphide | ,, |
| Ether | almost complete. |
| Oil of turpentine | 94·28 % soluble. |
| Petroleum ether | 84·95–97·60 % sol. |

The author's figures are—

| | |
|---|---|
| Acid value (direct) . . . . | 151·18–159·13 |
| Ester value . . . . . | 12·03– 27·31 |
| Saponification value (hot) . . | 163·23–179·94 |

While later determinations gave—

| | |
|---|---|
| Acid value (direct) . . . . | 149·80–155·35 |
| Ester value . . . . . | 12·64– 29·40 |
| Saponification value (hot) . . | 165·11–179·67 |

Together with the following acetyl values—

| | | |
|---|---|---|
| Acetyl | Acid value . . . . | 155·27–158·48 |
| | Ester value . . . . | 64·38– 75·48 |
| | Saponification value . . . | 222·86–230·75 |

(For the significance of these values, see *Chem. Rev.*, 1898, No. 10.)

With the exception of Kremel's figures the values are fairly concordant, showing that this means is of no more use for differentiating the various kinds of *Resina Pini* than it is for the turpentines (*q.v.*).

According to Maisch, artificial products, made of white pitch, oil of turpentine, and oil of wormwood, are met with in commerce. For the detection of pine resin and colophony in other resins by the Storch-Morawski reaction, see Colophony.

**The Resin of the Pine (Pinus abies)** has been investigated by P. Klason and J. Köhler, who separated from it two distinct isomorphous acids which they designated as $\alpha$- and $\beta$-colophonic acids, having the formula $C_{20}H_{30}O_2$ and an acid number of 185·4. The acids were not obtained in an absolutely pure state but were sufficiently pure to distinguish them from each other. Their characters were: $\alpha$-colophonic acid, crystallises from alcohol in colourless

oblique monoclinic prisms, M.P. 177°–182° and specific rotation $[a]_D$ — 59·41°; $\beta$-colophonic acid is in less well-defined crystals, M.P. 168°–173° and specific rotation $[a]_D$ + 52·2°.

**The Resin of the Red Fir (Picea excelsa)** has also been examined by J. Köhler, who found it to contain *l*-pimaric acid, which had previously only been obtained in an impure form from "gallipot." According to this author it is sometimes found in well-developed crystals in the "winter resin" obtained from the upper portion of the stem, but is usually accompanied by the more easily soluble acids (*e. g.* sapinic acids) of a lower rotatory power. The pure acid has the formula $C_{20}H_{30}O_2$ and a specific rotation at 20° of $[a]_D$ — 280·5°, and a melting point between 134°–152°, but the latter could not be accurately determined owing to a change taking place into colophonic acids. On heating it yields both lævo, dextro, and inactive colophonic acid. The winter resin is sometimes accompanied by a yellow liquid which has acid characters and quickly becomes partly crystalline. This oil is regarded as an aldehyde or camphor-like substance having the formula $C_{10}H_{16}O$, which changes to resin acids by oxidation.

According to Schkateloff, it is probable that the many acids which have from time to time been separated from the ordinary turpentines and from colophony are either identical with $\alpha$-sylvic acid or are derived from it by some form of transformation. He was able to isolate this acid in a pure state from the oleo-resins of *Pinus sylvestris*, *P. maritima*, *P. taurica*, and *P. strobus*. S. Leskiewicz has also examined the oleo-resin of *P. sylvestris*, and by frequent recrystallisation from acetone and alcohol, and not allowing the temperature ever to rise above 60°, he has easily succeeded in preparing the acid in a crystalline

form. The formula of the acid is $C_{20}H_{30}O_2$, but the latter author prefers to call it sapinic acid. The acids separated from the oleo-resin of *P. sylvestris*, the colophony of this oleo-resin, and also French colophony were, however, found to be different in their physical properties, as may be seen from the following figures:—

| | Acids from— | | |
|---|---|---|---|
| | Oleo-resin of *P. sylvestris.* | Colophony from *P. sylvestris.* | French colophony. |
| Melting point . | 142°–144° | 144°–146° | 146°–148° |
| Specific rotation . | at 19° — 105·3° | at 18° — 35·16° | at 19° + 14·21° |

and he is of opinion that the diminishing lævarotation and conversion to dextrorotation are due to the action of heat, less or more prolonged. Further details as to the action of acid and high temperatures are also given, the latter resulting in the production of the so-called colophonic acids.

The resin saps from various species of pine have been examined by W. Schkateloff, whose results are tabulated below:—

| Resin Sap. | *Pinus sylvestris.* | *Pinus abies excelsa.* | *Larix sibirica.* | *Pinus cembra.* | | *Pinus taurica.* | *Abies sibirica.* | *Pinus strobus.* |
|---|---|---|---|---|---|---|---|---|
| | | | | I. | II. | | | |
| Volatile oil, per cent. | 15–16 | 13·4 | 14·13 | 6·0 | 20·0 | 20 | 28 | Similar to that of ordinary pine |
| Specific gravity at 15° | — | 0·873 (19°) | 0·870 (15°) | 0·865 | — | 0·861 (19°) | 0·8751 (19°) | |
| Specific rotation $[\alpha]_D$ | + 22°–24° | — 13·2° | — 14·3° | + 14·04° | + 17° | — 75·9° | — 35·6° | |
| Acid present . . | α-sylvic | α-sylvic | β-sylvic | β-sylvic | — | α-sylvic | — | |
| M.P. of acid . . | — | 143° | — | — | — | — | — | |
| Specific rotation of acid $[\alpha]_D$ | — | — 74·1° | — | — | — | — | — | |

**Balsam of Pinus cambodgiana.**—The balsam of *Pinus cambodgiana* has been examined by Wickman. The product is honey-like in consistency, has a yellowish-grey colour and an aromatic odour. It is readily soluble in most solvents. The acid number (direct) is 145·31; indirect, 148·12. On steam distillation it yields 19·35 per

cent. of essential oil, specific gravity 0·892, and refractive index at 21° C. of 1·48455. The resinous portion yields cambopinic acid ($C_{11}H_{18}O_2$, M.P. 78° C.), cambopinonic acid ($C_{16}H_{24}O_2$, M.P. 71°), and also camboresene.

According to Bamberger and Landsiedl, pine resin consists of about 80 per cent. of material soluble in ether. This portion on saponification with alkali was found to be composed of the pinoresinol esters of abietic and paracoumaric acids, the former preponderating. The portion insoluble in ether had the properties of a resinotannol and has been named pinoresinotannol, $C_{30}H_{30}O_6(OCH_3)_2$.

Fir resin also yielded pinoresinol $C_{17}H_{12}O_2 . (OCH_3)_2 . (OH_2)$.

**Resin of Pinus laricio.**—According to M. Bamberger, the excrescent resin from this tree melts at about 100°. On dissolving in alcohol and passing a current of steam through the solution till all the alcohol is removed, a portion of the resin separates out but part of it passes into solution, separating on standing in the form of a crystalline crust. This substance was found to consist of caffeic acid with small quantities of ferulic acid, and vanillin.

**Resin of Pinus Jeffreyi.**—The resin of the Californian nut pine (digger pine), *Pinus Jeffreyi*, examined by A. Tschirch and C. Leuchtenberger, yielded the following acids: $\alpha$-jeffropinic acid ($C_{10}H_{14}O_2$, M.P. 160°–161°); $\beta$-jeffropinic acid ($C_{12}H_{18}O_2$, M.P. 80°–82°); $\alpha$-jeffropinolic acid ($C_{14}H_{20}O_2$, M.P. 117°–118°), and $\beta$-jeffropinolic acid ($C_{14}H_{20}O_2$, M.P. 77°–78°).

**Oleo-Resin of Pinus longifolia, etc., from India.**—In India, turpentine and resin are obtained from the "Chir" pine (*Pinus longifolia*) which grows in the Himalayas. The oleo-resin is distilled at the Government Station at Bhowali,

yielding 15½ per cent. of oil of turpentine and 67 per cent. of resin. At the new Jalloo distillery in the Punjab the yield of turpentine was slightly more than 22 per cent. The turpentine more nearly resembles Russian than American turpentine, and was valued at about half the price of the latter. More recently, however, the method of distillation has been considerably improved, and the product is now regarded as fully equal to American and French turpentine.

Several samples of the oleo-resin from pines have been sent to the Imperial Institute for examination, the results of their examination being as follows—

| | Crude Turpentine from Naina Tal. | Turpentine from *Pinus excelsa*, Punjab. | Turpentine from *Pinus Gerardiana*, Punjab. |
|---|---|---|---|
| Yield of oil, per cent. . . | 12·7 | 20·6 | 23·0 |
| Specific gravity at 15° . . | 0·8724 | 0·8613 | 0·8659 |
| Optical Rotation in 100 mm. tube | + 3° 7′ | + 35° 25′ | + 24° 54′ |

It is noted that the yield of turpentine would probably be greater in all cases from the fresh oleo-resin.

For the analysis of colophony from the same sources see p. 168.

**Hungarian Fir Resin.**—The resin of the fir (*Picea montana*, Schir.) is collected in parts of Hungary and sold locally in masses wrapped in the bark of the tree. It is stated by Augustin to yield a larger amount of resin than the spruce (*Picea excelsa*).

**Resin of Picea vulgaris.**—According to M. Bamberger, the excrescent resin melts at about 100°. When dissolved in alcohol and the solution heated by a current of steam until all the alcohol has distilled off and the solution

evaporated, a white crystalline substance separates which was proved to consist of para-coumaric acid [$C_6H_4$(CH = CH . CO . OH)(OH)] [1 : 4] and vanillin. No abietic acid was found in this resin, nor in that from *Pinus laricio*.

**Resin from the Cedar of Lebanon.**—Reutter and Schweinfurth have examined a sample of resin from the Cedar of Lebanon (*Cedrus Libani*). This had a faintly aromatic odour and melted at 95·5 to 97°. Acid value 54·5–58·6, ester value 0. A solution of alkali extracted two acids: cedric acid, $C_{10}H_{16}O_2$, a brownish-yellow amorphous substance, and cedrenolic acid ($C_{54}H_{86}O_5$), a semi-liquid product. The material insoluble in alkali consisted of a neutral unsaponifiable substance having the properties of a resene. The alkaline solution of the resin on distillation yielded a volatile oil having a specific gravity at 15° of 0·8802, refractive index at 20°, 1·48567, and a specific rotation of $[a]_D$ — 13·36°.

C. H. Herty and W. S. Dickson have estimated the amount of indifferent resenes in several pine resins after removal of the volatile oils. The amounts are given below:—

| Species. | Local name. | Origin. | Per cent. of resene. |
|---|---|---|---|
| Pinus Tæda . . . | Loblolly pine | N. Carolina | 4·10 |
| „ palustris . . . | Longleaf „ | Florida | 5·67 |
| „ maritima . . | Maritime „ | France | 7·37 |
| „ heterophylla . . | Cuban or Slash pine | Florida | 7·38 |
| „ serotina . . . | Pond pine | „ | 7·65 |
| „ echinata . . . | Old field pine | N. Carolina | 8·71 |
| „ species unknown . | — | Central America | 8·94 |
| „ sabiniana . . | Digger pine | California | 9·66 |
| „ laricio . . . | "Schwazkiefer" | Australia | 14·05 |

The resenes are also found in similar amounts in the natural oleoresins, so that they are not the result of the heat applied in separating the volatile oils.

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## 33. Rubber Resins.

India-rubber contains, besides caoutchouc, a greater or lesser proportion of resinous substances and other matters. The amount of resins present varies from 1·2 per cent. in the finest Para to as high as 63·9 per cent. in the variety known as African flake. These resinous products appear to have been formed at least in part by the spontaneous oxidation of the caoutchouc after its exudation from the tree, the action proceeding gradually in ordinary rubber exposed to air and light, thus leading to its becoming more brittle in course of time. The resin is known as Spiller's resin, and is regarded as having the formula $C_{30}H_{48}O_{10}$. It is supposed to be produced from polyprene $(C_5H_8)_n$, the hydrocarbon composing caoutchouc, by oxidation. There is no doubt that the quality of rubber varies inversely with the amount of resin present. The resins from several varieties of rubber and similar products have been extracted, and their properties determined, by F. W. Hinrichsen and J. Marcuson. Their action upon polarised light is generally dextrorotatory, but the rotation is lowered by vulcanisation (*i. e.* heating with sulphur), as the following figures serve to show:—

Optical Rotation of Resins

| | From Raw Rubber. Deg. | From Vulcanised Rubber. Deg. |
|---|---|---|
| Para | No action | No action |
| Ceylon | No action | No action |
| Equateur | — | + 7·1 |
| Guayale | + 12·5 | + 7·1 |
| Guayale | + 15·1 | — |
| Upper Congo | + 13·0 | — |
| Manaos | + 17·5 | — |
| Soudan sheets | — | + 17·1 |
| Kassai | + 29·8 | — |
| Peru | + 30·3 | — |
| Kickxia | + 32·9 | — |
| Dead Borneo | + 50·1 | — |
| Gutta-percha | + 46·7 | — |
| Balata | + 27·5 | — |

By heating with alcoholic potash the rubber resins are separated into two fractions, one of which is dissolved or saponified while the other remains unsaponified. The amount of unsaponifiable matter in the various resins is considerable, and the optical activity proves to be generally higher than that of the original material, as shown below :—

| | Per cent. Unsaponifiable. | Optical Rotation. Deg. |
|---|---|---|
| Para | 15·0 | 0 |
| Ceylon | 20·8 | 0 |
| Upper Congo | 56·6 | + 24·5 |
| Kickxia | 74·0 | + 27·5 |
| Guayale | 78·2 | + 27·9<br>+ 28·1 |
| Padang | 90·2 | + 40·1 |
| Kassai | 92·6 | + 34·5 |
| Dead Borneo | 100·0 | + 49·9 |

As polyprene or caoutchouc is optically inactive the authors come to the conclusion that there are two types

of resins present in the rubber. Those that are optically active they assume to be present in the latex *per se*, while the optically inactive ones are subsequently produced by the oxidation of the caoutchouc. The iodine values of the resins determined by the Hubl-Waller method were as follows:—

| | Iodine Value of Rubber Resins. |
|---|---|
| Dead Borneo | 30·6 |
| Padang | 87·1 |
| Guayale | 94·1 |
| Kassai | 107·0 |
| Para | 118·0 |

Dead Borneo or Pontianac is a remarkable product which can scarcely be regarded as a rubber, since it consists almost entirely of resinoid substances. A similar product to this has recently been examined by F. Jacobson. It is the product of a wild cotton tree (*Calotropis procera*), a native of the German East African Colony. It occurs as a whitish friable material, enclosing a considerable proportion of a colourless serum. The odour resembled that of some of the organic bases, and was rendered more evident by boiling with caustic potash, but on drying the odour was entirely removed. The product left after drying was sticky, non-elastic, and grey in colour, resembling some of the low-grade Venezuelan rubbers. Analysis of this product yielded the following figures:—

| | Original. Per cent. | After Drying. Per cent. |
|---|---|---|
| Water | 62·9 | — |
| Resins | 26·3 | 70·8 |
| Insoluble impurities (org. & inorg.) | 5·7 (mineral 2·4) | 15·3 |
| Rubber-like substance | 5·1 | 13·9 |
| | 100·0 | 100·0 |

The mineral matter contained alumina, ferric oxide, lime and magnesia.

The molecular weight of the rubber resin from Kickxia latex has been determined by Hinrichsen and Kindscher, using Raoult's freezing-point method, with the following result: ·2182 grm. of the resin dissolved in 23·9418 grms. of benzene lowered the freezing point 0·107° C., hence the molecular weight $= 5{,}000 \frac{\cdot 2182}{\cdot 107 \times 23 \cdot 9418} = 426.$

It is interesting to observe that while the formula $C_{30}H_{48}O_{10} = 568$, the molecular weight found by experiment is exactly three-quarters of this. A similar determination of the molecular weight of the rubber after allowing for the effect of the resin gave the figure 3173, which shows a highly complex molecule. $(C_5H_8)_{48} = 3128$, $(C_5H_8)_{47} = 3196$.

The resins may be extracted from rubber by means of acetone, and, according to Klassert, rubber resin is now extracted by this or similar means, and is offered for sale. It is a pale-coloured product, easily pulverised, and emitting an odour of raw rubber. It dissolves in most organic solvents on heating, but separates out again on cooling. Chloroform and carbon tetrachloride form the best solvents for the resin; the solutions leave dull films on evaporation. Rubber resin may be distinguished from ordinary resins by its chemical constants: acid value, 0; saponification value, 10; and iodine value, 28.

G. H. Hillen has recently given the results of his examination of the resins from a variety of rubbers. These resins, as previously stated, are extracted from rubber by means of acetone or other solvents in which the rubber is insoluble. They differ from ordinary resin in their low acid and saponification values, and in fact are not true resins in

the ordinary sense of the term. The proportion of resin in Jelutong or Pontianac rubber (*Dyera costulata*) is considerable. It is obtained in the form of a yellowish-white crystalline powder, which on examination was proved to consist of lupeol acetate, $\alpha$- and $\beta$-Amyrins, and a proportion of a resene.

The rubber of Manihot Glaziovii from German East Africa yields 7 per cent. of resins, containing isocholesteryl acetate, a green amorphous product, not readily soluble, and a dark-green syrupy substance.

Guayule Rubber. The sample examined was prepared specially, and contained only 16 per cent. of resins as against 24 to 30 per cent., the usual proportions. Phytosterols were absent from the sample, and no definite information as to the constituents could be obtained. The product is regarded as formed from essential oils by resinification.

Determinations of the proportion of resins extracted by acetone from a number of rubbers were made, and their microscopic appearance and reactions noted. The following figures were obtained :—

| Name of Rubber. | Per cent. of Resins. |
|---|---|
| Fine Para, from the Amazon | 2·1 |
| Congo root rubber (*Carpodinus*) | 5·0 |
| Vine (*Willoughbeia fuina*), from Malaya | 6·4 |
| Mangobeira (*Hancornia speciosa*), from Bahia | 7·04 |
| West Indian scrap (*Castilloa elastica*) | 7·9 |
| Kicksia (*K. elastica*), from German E. Africa | 8·8 |
| Landolphia (*L. camorensis*, var. *florida*), from German Camerun | 14·28 |
| Good Java rubber (*Ficus ?*) | 33·64 |
| Almeidina potato rubber (*Euphorbia ripsaloides*) | 79·8 |

A material from Pangalang (Metavi Islands) known locally as " Malabuwai," was found to be soluble in alcohol

with the exception of 10 per cent. The extract contained $\alpha$- and $\beta$-amyrin, traces of a yellow resene, and an oily product similar to that found previously in Chile gum by other chemists.

**Commercial Rubber Resins.**—W. Vaubel and E. Diller have examined seven samples of rubber resins. These products are now systematically extracted from the commoner grades of rubber by means of solvents for the purpose of increasing the value of the rubber. They pass under a variety of names, but they are not at all like common resin, and it is questionable if they have any right to the name of resins, since they consist for the most part of neutral substances, and are more akin to the resenes or unsaponifiable substances which are present in all resins. The constants determined for these products were: melting point, 90°–125° C.; mineral matter, 0·54–2·16; acid number, 3·2–13·6; saponification number, 19·4–24·3; bromine number, 12·9–16·4; iodine value calculated from the latter, 20·2–41·5; specific rotation 60·2–69·6. It is difficult to see why the bromine number is determined, because in very few cases is this of any value, the action being almost invariably less marked than when iodine is employed as in the Hubl or Wijs tests. These investigators dissolve the resin in benzene, add a solution of potassium bromate and hydrochloric acid, then potassium bromide, and titrate the excess of bromine by means of thiosulphate. Under these conditions the absorption of bromine is scarcely likely to be complete, as the solution of the resin in benzene, and the reagent will form two separate layers.

Klassert draws attention to the fact that a resin obtained from raw rubber has now become an article of commerce. This substance is pale coloured and has a conchoidal fracture. It is completely soluble in cold chloro-

form and in carbon tetrachloride, and these solutions leave on evaporation films which are very resistent, but dull in appearance. The resin is easily pulverised, and the powder has the odour of raw rubber. It will probably be useful as an electrical insulating material, and becomes strongly electrical by friction. Rubber resin differs from other resins in its chemical properties. Acid value 0, saponification value 10, iodine value 28. The resin is not appreciably altered in composition by heating for some time at a temperature of over 100° C. This is an interesting product, and if it should be found suitable for use as a varnish it would, no doubt, be especially useful in those cases where acidity is detrimental, as, for instance, in the manufacture of vehicles for bronze colours, etc. It may be mentioned that patents have been granted to Flamant and Worms (English patent 20,896, 1908; French patent 382,571, 1907) for the separation of the resin from rubber, also to Joly (French patent 396,300, 1908). The amount of resin in india-rubber varies considerably. In the pure varieties of Para rubber only 1·3 per cent. is found, but in the more impure African as much as 41 per cent. has been found by Terry, while Weber found even as high as 64 per cent. The resin appears to be partly of the nature of alban, with a composition represented by the formula $C_9H_{12}O$, but india-rubber itself oxidises on keeping to form a hard resin. Polyprene, the hydrocarbon from which caoutchouc is supposed to be produced, oxidises spontaneously to an acid resin $C_{30}H_{48}O_{10}$, known as "Spiller's resin." Pontianac or "dead Borneo" is a very impure rubber containing about 80 per cent. of resinoid bodies soluble in acetone.

**Phytosterols from African Rubber.**—N. H. Cohen has separated and examined the resin from a sample of "euphorbia" rubber, which had the composition:

caoutchouc (true rubber), 5·5; resin, 70; water, 25·4; and 1·7 per cent. of other constituents. After treatment several times with boiling alcohol a slight white residue was left, which crystallised from acetone in prismatic crystals, melting at 235° C. The solution in chloroform gave a rotation of + 83·7° in 100 mm. tube, and on heating with alcoholic potash it yielded *b*-amyrol, melting at 194° C. The substance was proved to be *b*-amyryl acetate. The resin, soluble in alcohol, after drying melted at 110° C.; it forms shining crystalline scales, and has the composition represented by the formula $C_{40}H_{50}O \cdot 2H_2O$, though, owing to its reactions, it is assumed to be a mixture of two distinct substances. Lupeol was not found to be present, but a phytosterol was isolated having the formula $C_{24}H_{40}O \cdot H_2O$, separating in needle-shaped crystals. Dissolved in chloroform this showed a rotation of + 58·6°. In its characters and reactions the phytosterol approaches very closely to the isocholesterol obtained by Schultz from wool fat; if these should be identical, as suggested by the author, it would be of extreme interest, as up to the present time the cholesterols of animal fats and the phytosterols of vegetable fats have been regarded as perfectly distinct.

**Phytosterols of Castilloa and Ficus Rubber.**—According to Ultée, Castilloa caoutchouc contains about 20 per cent. of resinous bodies from which alcohol extracts *b*-amyrin acetate, melting at 184°–188° C.; another acetate also present melted at 121°–122·5° C. The caoutchouc obtained from Ficus also contains a resin which on extraction yielded a substance melting at 76°, this being also found in the Castilloa caoutchouc to a slight extent. *b*-amyrin acetate, melting at 218°, was also isolated, though these substances are not present to any very great extent.

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## 34. Sandarach.

*Resina Sandaraca.*

**Origin and Habitat.**—*Callitris quadrivalvis* (Coniferæ). North-west Africa. (For the Australian sandarachs, see end of section.)

**Chemical Constituents.**—Sandaracolic acid ($C_{44}H_{65}O_5$-COOH), 85 per cent.; callitrolic acid ($C_{64}H_{82}O_5$ (OH) COOH), 10 per cent.; ethereal oil and bitter principle, 2·84 per cent.; water, 0·56 per cent.; ash, 0·1 per cent.; impurities, 1·5 per cent. (Balzer).

Tschirch and Wolff recently succeeded in isolating new "resinol acids," etc., from sandarach by fractional separation with ammonium carbonate and sodium carbonate. (Compare Dammar, and see also *Ph. Ztg.*, 1899, No. 77.)

These are sandaracic acid ($C_{22}H_{34}O_3$, M.P. 186°–188°), 2·3 per cent.; sandaracinolic acid ($C_{24}H_{36}O_3$, M.P. 265°–275°); sandaracopimaric acid ($C_{20}H_{30}O_2$, M.P. 170°); and a third acid, together 87 per cent.; ethereal oil (B.P. 152°–159°), 1·3 per cent.; sandaracoresene ($C_{22}H_{36}O_2$, M.P. 57°), 3·3 per cent.

T. A. Henry found two acids to be present, inactive pimaric acid ($C_{20}H_{30}O_2$) and callitrolic acid ($C_{30}H_{48}O_5$), together with a small quantity of an essential oil.

**General Properties and Commercial Varieties.**—Ordinary African (Morocco) Mogador sandarach occurs in the form of somewhat elongated, yellowish lumps, which are dusty on the outside, and break down into powder when

chewed, instead of softening—thus differing from mastic. It is completely soluble in alcohol and ether, but only partially in carbon di-sulphide, chloroform, oil of turpentine, and petroleum ether, and less soluble in benzol. Australian and Tasmanian sandarach (from other kinds of *Callitris*) and West Indian sandarach (which is of doubtful origin) are practically out of the market. This remark also applies to the so-called "German" sandarach, a granular resin occasionally found under the bark of the juniper. A few varieties of sandarach—*e. g.* Australian—are found as "soft copal" in commerce.

**Adulterants.**—Mastic, colophony (especially in powder), Resina Pini, and dammar.

**Analysis.**—African sandarach being the principal commercial variety, whereas Australian sandarach is only met with in isolated parcels, the analytical data of the former is the more important.

It may be premised that—as in the case of copal—the different age of the samples must be responsible for the divergent and often very contradictory results obtained. This applies to the degree of solubility in alcohol, ether, benzol, or petroleum ether, as well as to the acid value and specific gravity.

Williams found—

| | I. | II. |
|---|---|---|
| Acid value (direct) | 154·0 | 145·6 |
| Saponification value | 155·4 | 157·0 |
| Iodine value | — | 134·30 |
| Ash | 1·88 per cent. | 1·44 per cent. |
| Loss at 100° C. | 0·04 „ | 0·17 „ |

The ester value was so low that Williams remarked the large amount of free acid as compared with the small quantity of esters.

Von Schmidt and Erban found—

| | |
|---|---|
| Acid value (direct) | 141·4 |
| Saponification value | 174·4 |
| Iodine value | 66·8 |

and for the solubility—

| | |
|---|---|
| Alcohol | soluble. |
| Ether | ,, |
| Methyl alcohol | partially soluble. |
| Amyl alcohol | soluble. |
| Benzol | almost insoluble.[1] |
| Petroleum ether | insoluble. |
| Acetone | soluble. |
| Glacial acetic acid | partially soluble. |
| Chloroform | ,, ,, |
| Carbon di-sulphide | almost insoluble. |
| Oil of turpentine | partially soluble. |

Flückiger's results are as follows :—

| | |
|---|---|
| Pure absolute alcohol<br>Ether<br>Amyl alcohol<br>Acetone | completely soluble. |
| Chloroform | partially soluble. |
| Ethereal oils | ,, ,, |
| Benzol | insoluble.[2] |

C. Coffignier has also determined the solubility of sandarach, and found :—64·20 per cent. soluble in methyl alcohol, 82·20 in acetone, 81·80 in benzaldehyde, and completely soluble in aniline.

For the solubility of sandarach in epi- and di-chlorhydrin (Valenta), see Table in Part I.

[1] See note on Flückiger's observations.

[2] As stated by von Schmidt and Erban, sandarach is only partially insoluble in benzol, the author having found up to 40 per cent. soluble (See "Adulterated Sandarach.") A specimen entirely insoluble in benzol is, according to existing experience, a rarity.

Hager found the specific gravity to be :—1.078–1·088

Kremel found—

| | |
|---|---|
| Acid value (direct) . . . | 144·20 |

Mills and Muter state that the saponification value is 164 and the bromine value 96·4.

A. Rudling gives the following figures :—

| | |
|---|---|
| Water . . . . . | 2·00 |
| Insoluble in alcohol . . . . . | 0·54 |
| Acid value . . . . . | 137·2 |
| Saponification value. . . . . | 152·4 |
| Iodine value . . . . . | 91·8 |

E. Dieterich gives the following :—

| | |
|---|---|
| Acid value (direct) . . . | 97·53–123·20 |
| Soluble in chloroform . . . | 23·15 per cent. |

The ester and saponification values quoted by this author are omitted, sandarach being free from esters.

Hirschsohn found—

| | |
|---|---|
| Soluble in petroleum ether . . | 7·0–8·0 per cent. |

The author is of opinion that the only way to ensure complete combination of the resin acids, in the examination of sandarach, is by indirect titration. In this method it is unnecessary to dissolve the resin beforehand, the alkali acting as a solvent, as well as combining quantitatively with the resin acids; moreover, the colour-change from red to yellow is much more noticeable than the reverse change in direct titration.

The method of estimation is as follows :—

(*a*) *Acid value* (indirect).—One grm. of sandarach is treated with 20 c.c. of alcoholic $\frac{n}{2}$ potash and 50 c.c. of benzine (sp. gr. 0·700), it is then left for twenty-four hours in a tightly closed vessel, at the end of which time the contents are titrated back with $\frac{n}{2}$ sulphuric acid, without addition

of water. The volume (c.c.) of KHO combined, multiplied by 28·08, gives the acid value.

(*b*) Ash determination.—Two grms. of sandarach are carefully incinerated, and calcined until it becomes constant in weight.

Preliminary experiments showed that alcoholic alkali used alone is preferable to mixed alcoholic and aqueous potash, it is also simpler in practice though there may be but little difference in the resulting values. Moreover, direct titration gave lower and less concordant values, and a less precise colour-change at the end-point. Finally, the indirect titration method obviates the necessity of preparing a solution of the resin previous to adding the standard alkali.

The following values (in round numbers) were furnished by numerous specimens of African sandarach :—

*Mogador* (*Morocco*) *sandarach*—

| | |
|---|---|
| Acid value (indirect) . . . . . | 130–160 |
| Acid value (direct) . . . . . | 90–110 |
| Ash . . . . . | *nil* |

the author would therefore specify that a pure sandarach should be practically free from ash, in addition to giving the above acid values, direct or indirect as the case may be.

With regard to the differentiation of sandarach from mastic, the higher acid value (indirect) of the former affords a means to this end; moreover, sandarach pulverises when chewed, whereas mastic softens, the latter is also soluble to a greater extent in benzol. Furthermore, according to Mauch, sandarach is practically insoluble in 60 per cent. chloral hydrate, in which mastic is partially soluble, both being soluble in the 80 per cent. solution of this reagent. Mastic is more readily soluble in oil of turpentine than sandarach. Adulteration with colophony or Resina Pini raises the acid

value, and considerably increases the percentage soluble in petroleum ether, whilst dammar, with its low acid value, depresses this constant. For the detection of colophony by the Storch-Morawski reaction, see Colophony.

The author has reported as follows, on the examination of an adulterated sandarach :—

" The adulterated specimen could not be distinguished from pure sandarach by its outward appearance, so that buyers who, as unfortunately is the general custom, purchase by the appearance only, would not have noticed anything in the least degree remarkable about it. Also, the qualitative solubility in alcohol, ether, benzol, and petroleum ether did not, at first sight, appear abnormal. The quantitative examination, however, was far more elucidating; the adulterated specimen examined in the author's laboratory, by H. Mix, furnishing the subjoined interesting values :—

| | | |
|---|---|---|
| 1. | Soluble in 60 per cent. chloral hydrate solution | 6·80 per cent. |
| 2. | Insoluble in 60 per cent. chloral hydrate solution | 93·20 ,, |
| 3. | Insoluble in petroleum ether | 6·89 ,, |
| 4. | Soluble in petroleum ether | 93·11 ,, |
| 5. | Insoluble in benzol | 2·74 ,, |
| 6. | Soluble in benzol | 97·26 ,, |
| 7. | Acid value (indirect) | 173·98<br>175·50 |

" On the other hand, pure sandarach, according to Mauch, is practically insoluble in the above chloral hydrate solution (we found up to 4 per cent. soluble). In benzol, sandarach is almost insoluble, according to von Schmidt and Erban, or quite insoluble, according to Flückiger; but the author cannot confirm the great pharmacologist's results in this respect, having, like von Schmidt and Erban, found a portion to be soluble—in fact in some cases up to more than 40 per cent. (see below).

" According to Hirschsohn, the solubility of pure sandarach

in petroleum ether does not exceed 8 per cent. The author's researches, so far, show the normal acid value of sandarach to be about 140. As colophony considerably raises the acid value, and is also much more soluble than sandarach in chloral hydrate, benzol, and petroleum ether, the above values given for adulterated sandarach clearly show that the specimen was an artificial mixture of sandarach and colophony. The adulterated sample was also more readily soluble in alcohol than the pure drug. Finally, Haberlé succeeded in isolating from the falsified product the characteristic resin acids of colophony.

"It should be mentioned that the adulteration had been so cleverly manipulated that only the above accurate quantitative testing revealed the true nature of the product.

"The discoveries of Haberlé, the appearance of the specimen, which agreed exactly with that of Mogador sandarach, and the circumstance that the goods were designated real sandarach, precluded the possibility of its being some other kind of sandarach of unknown origin. Australian sandarach was also ruled out of question by the fact that its acid value is never so high as that of true sandarach."

The more recent methods of examination have also been applied to sandarach, the author having, for example, determined the acetyl values—

| | | |
|---|---|---|
| Acetyl | Acid value . . . . | 166·03–169·83 |
| | Ester value . . . . | 73·59– 81·60 |
| | Saponification value . . . | 239·62–251·43 |

Kitt found the following carbonyl values: = 0·43–0·74.

Gregor and Bamberger found the methoxyl value to be *nil*, notwithstanding that Tschirch and Balzer have shown the presence of a methoxyl group in sandaracolic acid.

(For the worth of these last-named determinations, see *Chem. Rev.*, 1898, No. 10.)

In conclusion, the results obtained up to the present with Australian varieties of sandarach may be given (compare Maiden's valuable treatises cited in the Bibliography at foot). This authority gives the following particulars with regard to the origin, properties, etc., of Australian sandarachs :—

*Callitris cupressiformis*, Vent.—This is found growing all over Australia, except in West Australia, and is one of the best-known species. The resin is water-white, transparent, and clear ; on prolonged storage it assumes a slight coloration, without, however, losing any of its lustre.

*C. calcarata*, R. Br.—Found in the territory from North Victoria to Central Queensland. The resin is pale yellow, and thickly coated with flowery dust. Is insoluble in water, but soluble in alcohol, leaving only a small whitish residue. Petroleum ether dissolves out 5 per cent. of a perfectly colourless transparent resin. A second very fine specimen, pale yellow in colour, and with an excellent aroma, was soluble in alcohol, with the exception of 1·3 per cent. of residue, and furnished a pale yellow and perfectly clear solution. Petroleum ether took up 22·1 per cent. A third sample proved of quite different character. It had the consistence and general constitution of Manila elemi, but differed from this substance by its flesh-tint colour and purely turpentine smell. The sample was the more remarkable from the fact that the same tree also yielded sandarach of the ordinary colour.

*C. columellaris*, F. v. M.—New South Wales and Queensland. The resin is rather pale in colour ; alcohol dissolves 95·4 per cent. to a pale yellow solution ; petroleum ether, 35·8 per cent. to a clear, colourless liquid. This high degree of solubility, as compared with all other kinds of sandarach, in petroleum ether is specially noteworthy.

*C. verrucosa*, R. Br.—Botanical Garden, Sydney. Very

dark resin, soluble to the extent of 97·5 per cent. in alcohol, and 22·8 per cent. in petroleum ether. The same variety was formerly reported on by Morel, and consisted of pale yellow tears, thicker and longer than ordinary sandarach, covered with white dust, and of agreeably aromatic odour, with bitter aromatic taste.

Supplementing the labours of Maiden, Clarke stated that Mogador (*i. e.* African) sandarach is better and purer than Australian. This may be the reason why the latter has not been more utilised.

In addition to the foregoing general properties and solubilities, the following analytical data on Australian sandarach have been published by the author. The acid values alone were determined, the indirect method, already described, being employed :—

| | | I. | II. |
|---|---|---|---|
| | | Acid Value (indirect). | |
| Australian sandarach | . . . | 139·00 | 139·00 |
| Do. | fine selected . | 129·87 | 130·57 |
| Do. | seconds . . | 144·61 | 144·61 |
| Do. | ordinary . . | 155·84 | 157·28 |

According to these figures, the acid values of the best Australian sandarachs are not as high as those of the African product; nevertheless, great similarity exists between the two kinds.

Richard T. Baker and Henry G. Smith, in their monumental work on *A Research on the Pines of Australia*, refer to the sources of Australian sandarach and give a considerable amount of information about the resin.

The trees from which it is obtained are *Callitris calcarata* (black pnie), *C. glauca* (white pine), *C. arenosa* and others. The resin, which closely resembles the African sandarach, is contained in the form of an oleo-resin in the cells of the inner back, and exudes in the form of tears when the outer

bark is punctured. A certain amount of the resin has been exported to this country under the names of " pine gum," " pine resin," " white pine resin," and " Cypress pine resin."

The collection of this product is not carried on systematically, but up to the present time the greater part obtained appears to have been derived from *C. glauca* and *C. calcarata*, the two species which are most widely distributed in New South Wales. The authors found two acids to be present, easily distinguished by the fact that the potassium salt of the one is insoluble in an excess of alcoholic potash, whereas the other is soluble. There was also a small quantity of an essential oil present. The acid value of the resin from *C. arenosa* is 154 as compared with 151 for commercial sandarach. The specific gravity varied between 1·069 and 1·079 at 16° C., but a freshly exuded sample from *C. Tasmanica* had the low gravity of 1·058, which appears to show that the gravity increases with age. The optical rotation of sandarach is slightly dextrorotatory, the following figures being given for a solution of 1 grm. of the resin in 5 c.c. of acetone examined in a 100 m.m. tube.

| Resin from | Rotation. | Mean Specific Rotation. |
|---|---|---|
| Callitris calcarata . . | + 5·9° to + 6·1° | $[a]_D$ = + 30·08° |
| ,, glauca . . | + 6·9° to + 8·7° | + 36·5° |
| ,, rhomboidea . | + 7·6° | — |
| ,, arenosa . . | + 6·7° to + 6·8° | + 38·8° |
| ,, Tasmanica . | + 6·1° | — |
| ,, verrucosa . | + 6·4° to + 9·4° | — |
| ,, Macleayana . | + 8·1° | — |
| ,, oblonga . . | + 7·6° | — |
| Sandarach :— | | |
| First quality, N. Africa | + 5·8° | |
| Second quality ,, | + 5·1° | + 27·66° |
| Mogador . . . | + 5·7° | |

For Asia Minor sandarach the author found—

| | |
|---|---|
| Acid value (indirect) . . . . | 179·01–179·71 |

The pure resin acids from African sandarach in two estimations showed the acid values, 141·10 and 141·10, which agree with the average furnished by natural sandarach, and preclude the presence of any esters or neutral substances.

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## 35. Scammonium.

*Resina Scammonium.*[1]

**Origin and Habitat.**—*Convolvulus Scammonia*, L. (Convolvulaceæ). Aleppo, Smyrna.

**Chemical Constituents.**—Since both the Aleppo and Smyrna varieties are very impure, the product (Resina scammonium) artificially prepared from the roots is generally vended and used.

The chief constituent is Scammonin $C_{34}H_{56}O_{16}$, which, according to Spirgatis, is identical with Jalapin or Orizabin.

According to A. Goris and G. Fluteaux, natural scammony contains :—moisture, 5; ash, 7·18; matter soluble in 95 per cent. alcohol, 79·52; insoluble in alcohol, 8. The amount soluble in ether was 66·7 per cent. The specific

[1] More precisely speaking, the Aleppo Scammonium should be called " juice," and that recovered from the root, " resin."

rotation of the resin soluble in alcohol was $[a]_D = -21{\cdot}47°$, and that soluble in ether $-24{\cdot}26°$.

**General Properties and Commercial Varieties.**—Aleppo scammonium, or "usu Aleppo," is in the form of light, opaque, rough lumps, with edges more or less sharp, and of a greenish ashy grey colour. The fracture shows a faint waxy but not greasy lustre; the flavour is very disagreeably irritant; the resin forms an emulsion with water.

Scammonium "in tears," a very pure variety, is no longer in the market.

Smyrna scammonium forms dense, heavy lumps or cakes, of a dark, almost black, colour, and waxy-lustrous fracture; the resin does not emulsify in water. Aleppo scammonium in its pure state (see below) is more valuable than the Smyrna variety.

French scammonium, from *Cynanchum acutum*, is no longer met with in commerce.

All varieties of scammonium, particularly that from Aleppo, being very impure, the natural resin is usually replaced, for pharmaceutical purposes, by "Resina scammonium," prepared from the root of *Convolvulus Scammonia*. It appears in the form of lumps or sticks, dull on the outside but lustrous on the surfaces of fracture; is soluble in alcohol, and has an aromatic odour.

With regard to the resin from *Convolvulus althæoides*, see Resina Jalapa.

**Adulterants.**—Artfiicial products, consisting of chalk, resin, colouring matters, and extractives, containing as much as 50 per cent. of mineral substances.

**Analysis.**—Aleppo scammonium is a resin that has always been subjected to more adulteration than probably any other known kind; for which reason it was necessary to replace it in pharmacy by the resin obtained from the

roots aforesaid. The following communication made by Thompson may be cited to show the almost unexampled adulteration practised on scammonium. An alleged scammonium received by this authority exhibited little claim to be considered pure, even under external examination. Nevertheless it was labelled, "Scammonium containing 84 per cent. of scammonium," the formula $C_{32}H_{56}O_{16}$ being appended. The specimen, which is said to have come from a German firm of drug merchants, consisted of irregular, greenish black, hard, horny lumps, with a resinous fracture, difficult to pulverise, and contained—

| | |
|---|---|
| Soluble in ether | 0·4 per cent. |
| Soluble in alcohol | 2·0 ,, |
| Soluble in water | 42·6 ,, |
| Starch, and a little cellular matter | 43·0 ,, |
| Moisture | 12·0 ,, |

On combustion there remained 2·12 per cent. of ash (43·6 per cent. of which was soluble in water) containing potassium, magnesium and calcium, in the form of carbonates and sulphates, together with a trace of chlorides, silica, and oxide of iron. The portion soluble in water was nothing but gum arabic, the insoluble matter consisting of starch and a little cellular tissue. H. Greenish also reports on the multifarious adulterations of Aleppo scammonium with starch, wood ashes, soil, gum, tragacanth, powdered roots, etc. Rebner examined five commercial varieties of "Resina," and found one of them to be entirely soluble in ether, the solubility of the others being 26, 40, 78, and 79 per cent. respectively. Three of these contained starch.

R. Squibb in his examination of upwards of thirty samples found the amount soluble in ether to vary from 25–79·7 per cent. According to the *Brit. Pharm.*, the resin should

contain not more than 3 per cent. of ash and 70 per cent. at least soluble in ether.

Christison found 15–38 per cent. of carbonate of lime in chalky kinds, and 13–42 per cent. of impurities in the amylaceous specimens.

Hess examined the following kinds of scammonium :—

| | Sp. gr. | Water. |
|---|---|---|
| I. fusc. Ph. G. . . . | 1·142 | 2·2 % |
| II. alb. . . . . | 1·107–1·112 | 4·5 % |
| III. Ph. G. . . . . | 1·104–1·110 | 4·0 % |
| IV. Ph. Holl. . . . | 1·120 | 5·4 % |
| V. Ph. Suecic . . . . | 1·160 | 4·3 % |

He recommended the use of the root resin purified with bone black, and insisted that this resin should be perfectly soluble in cold alcohol. According to Mœller, Aleppo scammonium should not contain over 8 per cent. of ash—a condition fulfilled by few of the highly adulterated samples now obtainable. The consensus of experience is in favour of the introduction of the resin prepared from the root, to replace the impure and worthless Aleppo scammonium.

The root extract is prepared by exhausting the powdered root with strong alcohol, the product being purified with charcoal if required. According to E. Dieterich, the yield obtained is about 10 per cent. Dœnsch published a report on the *Resina scammonium* extracted from the root, and found the yield to be slightly over 5 per cent. of (repeatedly purified) resin. On the other hand, three commercial samples behaved differently, and furnished an ash which was not perfectly soluble in dilute hydrochloric acid. The acid solutions contained lime in some cases, magnesia in others. The impurity of the commercial products is probably the cause of the difference in the behavour of the ash, etc., in comparison with the pure scammonium

prepared in the laboratory. In any case, the commercial "Resina" prepared from the root is of much greater purity than Aleppo scammonium.

Isolated instances of acid value (direct), ester value, and saponification value determinations are to be found in the literature of the subject. According to G. Weigel, the acid value of scammony is never more than 30.

Kremel found (by the usual method)—

| | Aleppo Scammonium. | "Resina" Scammonium. |
|---|---|---|
| Acid value (direct) . . . | 8·2 | 14·6 |
| Ester value . . . . | 172·0 | 171·0 |
| Saponification value (hot) . . | 180·2 | 185·6 |

From these figures it would seem that Kremel had a very pure specimen of Aleppo scammonium to deal with, since the values are almost the same as those for the extracted resin.

E. Dieterich determined only the iodine value; Gregor and Bamberger the mexthoxyl value, which they found to be *nil*.

Two samples of Mexican scammony and also the resin extracted from the drug have been examined by W. B. Cowie and B. M. Brander, who give the following results:—moisture, 2–3·05 per cent.; ash, 0·16–0·20 per cent.; acid value, 8·4; saponification value, 295–327; soluble in ether of 0·720 sp. gr., 68·6–72 per cent.; melting point, 100° C.; rotatory power $[a]_D = -18{\cdot}75°$ to $-27°$. Although Flückiger stated that the resin is completely soluble in ether and insoluble in carbon bisulphide, the authors found this not to be the case, the amount soluble in carbon bisulphide being 4·8 per cent. They examined both the resins soluble and insoluble in ether and carbon bisulphide. The saponification value of the ether-soluble resin was 333, and its melting point

103° C., while the ether-insoluble portion had a saponification value of 357 and a melting point of 113°. The portion soluble in carbon bisulphide melted at 75° and the insoluble portion 115° C.

W. B. Cowie has examined several samples of scammony resin, with the following results :—

| | White Scammony Resin. | | Pure Scammonin. | Pure Brown Scammonium. | |
|---|---|---|---|---|---|
| | I. | II. | | I. | II. |
| Moisture | 2·52 | 5·3 | — | 4·5 | 5·1 |
| Ash | 0·02 | — | — | 0·15 | — |
| Acid value | 2·8 | — | 2·8 | 25·2 | 28 |
| Saponification value | 241 | — | 240 | 263 | — |
| Optical rotation $[\alpha]_D$ | − 25° | — | − 25° | — | — |
| Soluble in ether | Complete | — | — | — | — |
| Melting point | 120° | — | 130° | — | 100° |

He states that 1 grm. of white scammonin should be completely soluble in 15 c.c. of ether of 0·720 sp. gr., and that 95 per cent. of the brown resin should be soluble. The limit for acid value he fixes at 8·4 for the white resins and 34 for the brown.

P. Guignes suggests the determination of the optical rotation as a means of determining the purity of scammony, using an ethereal solution, and gives the following values :— Scammony, maximum − 24° 30′ for resin extracted from the gum resin, and − 18°–30′ to −23° 30′ for resins extracted from the roots. Commercial Tampico jalap gave − 34° 20′; true Orizaba jalap − 24° 45′; officinal jalap −36°; officinal turbith − 30° 10′ to −31° 35′; ordinary colophony + 6° to + 7°; sandarach from the Arabic bazaar + 46° 20′; pure sandarach + 31° to + 34°; recent mastic + 29° 30′, second quality mastic + 21° 50′; guaiacum − 17°.

Only Orizaba jalap and guaiacum could be used as adulterants, both of which could be detected by other tests.

F. O. Taylor gives the following figures for pure scammony resin, also of "Mexican scammony" and for samples which are presumed to be mixtures of the two.

| | Yield of Resin from Root. | Moisture. | Ash. | Soluble in Ether. | Acid Value. | Saponification Value. | Iodine Value. |
|---|---|---|---|---|---|---|---|
| True scammony (?) . | 8·1 | 2·18 | 0·12 | 99·0 | 21·1 | 232·4 | 13·3 |
| ,, ,, (?) . | — | 2·09 | 0·15 | 98·8 | 14·5 | 232·8 | 10·5 |
| ,, ,, . | 7·93 | 1·71 | 0·05 | 99·7 | 15·6 | 238·1 | 10·8 |
| ,, ,, . | 8·06 | 1·74 | 0·09 | 99·3 | 18·2 | 238·0 | 13·0 |
| ,, ,, . | 8·52 | 1·65 | 0·20 | 99·0 | 21·3 | 239·4 | 14·6 |
| Mexican scammony . | 16·75 | 1·77 | 0·09 | 99·6 | 15·5 | 186·6 | 8·7 |
| ,, ,, . | 16·83 | 2·03 | 0·22 | 96·5 | 21·5 | 187·1 | 11·5 |
| ,, ,, (mainly) | 12·2 | 1·94 | 0·08 | 99·5 | 14·6 | 198·4 | 8·7 |

In their investigations Evans' Sons, Lescher & Webb found a considerable amount of variation in the proportion of resin soluble in ether, the figures ranging from 46–86 per cent., and they give the following figures for several samples examined by them:—

| | Resin Content. | Acid Value. | Ester Value. | Saponification Value. | Iodine Value. |
|---|---|---|---|---|---|
| 1. | 50 per cent. | 7·8 | — | — | 6·7 |
| 2. | 60 ,, | 7 | 237·5 | 244·5 | 7 |
| 3. | 66 ,, | 7 | 233 | 240 | 3·6 |
| 4. | 70 ,, | 8 | 239·9 | 247·9 | 6·1 |
| 5. | 74·6 ,, | 7·6 | 242·7 | 250·3 | 9·6 |
| 6. | 76·4 ,, | 8·4 | 241·6 | 250 | 4·5 |
| 7. | 80 ,, | 7 | 223 | 250 | 5·9 |
| 8. | 85 ,, | 9 | 239·4 | 248·4 | 4·7 |
| 9. | 100 ,, | 12 | 238·0 | 250 | 5·3 |

They remark on the very high ester values and low iodine values as being characteristic for this drug.

Messrs. Evans' Sons, Lescher & Webb have also examined several samples of Orizaba scammony resin; the figures

obtained, which agree on the whole with those of Weigel and Taylor, are intermediate between those of true Scammony resin (from *Convolvulus scammonia*) and jalap resin :—

| | Acid Value. | Ester Value. | Saponification Value. | Iodine Value. |
|---|---|---|---|---|
| 1. | 11·2 | 161·3 | 172·5 | 12·2 |
| 2. | 14·7 | 172·7 | 187·4 | 12·1 |
| 3. | 14·9 | 167·1 | 182·0 | 11·3 |
| 4. | 12·3 | 164·0 | 176·3 | 8·3 |
| 5. | 12·3 | 175·1 | 187·4 | 13·3 |
| 6. | 24·1 | 178·6 | 202·7 | 15·3 |

The alcoholic root extract (commercial " Resina scammonium ") should, in the first place, be soluble in alcohol without leaving any appreciable residue, and should not contain any notable proportion of ash. Aleppo scammonium is often used, instead of the root, for preparing " Resina," by a method of purification with alcohol and charcoal. From the point of view of the purity of the final product, this method cannot be recommended, the alcohol extracting the foreign resins (colophony, etc.) pre-existing in the Aleppo scammonium, which are therefore conveyed into the purified product,—an occurrence that is, of course, impossible in the case of the root. In view of the drastic action of scammonium, a maximum degree of purity is necessary in the " Resina," and the requirements should be made correspondingly stringent. Hooper believes that the variable percentage of resin in the roots is attributable to the condition of the soil, especially with regard to the percentage of phosphates.

For the detection of colophony in scammonium by the Storch-Morawski reaction, see under Colophony.

The resin should give no coloration with ferric chloride or hydrogen peroxide, as distinguished from guaiacum resin ; it is also entirely soluble in ether (difference from jalap).

Other resins are detected by yielding a precipitate with acids from alkaline solutions, scammony and jalap yielding no precipitate.

For detecting guaiacum resin in scammony, G. Weigel recommends dissolving ·5 grm. in 5–10 c.c. of alcohol and mixing with 20 c.c. of a solution of gum arabic in cold water; a blue colour is developed if guaiacum is present.

An instance of gross adulteration of scammonium is reported in the *Ap. Ztg.*, 1898, No. 47.

A sample of the drug tested on account of its suspicious appearance (it exhibited peculiar small cavities, interspersed with tiny grey and blackish blue metallic-looking crystalline spangles) was found, on extraction with ether, to contain 41·3 per cent. of resins, whereas good commercial specimens should exhibit 75–80 per cent. The ash content was 16·6 per cent. as against 3–8 per cent. in good scammonium. The residue, insoluble in ether, contained a large proportion of starch; and a considerable amount of lead sulphide was also detected. (*Petit Moniteur de la Pharmacie*, 1899, p. 3208.)

This dangerous adulteration recalls the equally dangerous artificial coloration of shellac with arsenic sulphide (*see* Shellac).

According to Bullough, jalap, scammony and podophyllin are insoluble in benzene, whereas other resins are all more or less soluble.

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## 36. Shellac.

*Resina Lacca.*

**Origin and Habitat.**—Product of the lac insect (*Coccus Lacca* Keor), parasitic on—*Croton lacciferum*, or Bihar tree (Euphorbiaceæ); *Ficus religiosa*, or Pepel tree (Artocarpeæ); *Butea frondosa*[1] and other varieties of Butea (Papilionaceæ); and on *Chenopodium anthelminticum* (stinking weed). Ceylon Antilles, Farther India.

**Chemical Constituents.**—Wax (M.P. 59°–62°), 6 per cent.; laccin pigment, 6·5 per cent., with laccinic acid $(C_{16}H_{12}O)_8$; pure resin, 74·5 per cent., of which 35 per cent. is soluble in ether and contains an odoriferous principle, a portion of the resinous substance, and erythrolaccin. The remaining 65 per cent. of the pure resin is insoluble in ether, and contains the resinotannol ester of aleuritic acid. (The formula of this acid is $C_{13}H_{26}O_4$, M.P. 101·5°.) The instability of the resinotannol has hitherto rendered a close investigation impossible. The impurities comprise sand, fragments of wood, etc., 9·5 per cent.; water, 3·5 per cent. (Farner).

Gascard found the wax of shellac to contain 50 per cent. of free myricyl alcohol, a smaller proportion of ceryl alcohol, and also esters of melissic, creotic, oleic, palmitic, and a nitrogenous resin acid with these alcohols. R. Benedikt and F. Ulzer have also examined the wax with somewhat similar results.

**General Properties and Commercial Varieties.**—The sticklac is deprived of its pigmentary matter, which then comes into commerce as "lac dye." The resinous residue is vended as *Lacca in tabulis* (scales) or *Lacca in granis* (granular), according to the colour. Button lac and garnet

[1] This gum lac, from *Butea*, should not be confounded with Bengal kino; also from *Butea frondosa*, which resin is obtained from the tree trunk.

lac are adulterated varieties. The perfectly white bleached lac is met with in commerce as *Lacca alba*, in the form of twisted striated sticks, and is the purest and most free from colouring matter, although it contains water and has been more or less altered in its nature by the bleaching agents. The colour of the foregoing grades varies between white and dark reddish brown. As is well known, shellac is largely used in varnish-making.

The so-called "Arizona shellac" or "Sonora gum" comes from *Larrea Mexicana* (Zygophylleæ). On the other hand, according to Hartwich, *Mimosa lacciſera* furnishes a "Sonora gum," produced as a granular lac by the insect *Carteria Mexicana*.

**Adulterants.**—Colophony, aloe resin, arsenic sulphide, orpiment.

**Analysis.**—Colophony, and other cheap resins (also aloe resin), being used to adulterate shellac, particular attention has been devoted to the solubility of shellac in alcohol, petroleum ether, and ether.

Hirschsohn tested the solubility of numerous specimens in petroleum spirit, both cold and hot, and obtained the following results :—

| | Per cent. soluble— | |
|---|---|---|
| | Dried at 17° C. | at 120° C. |
| 1. Lacca in baculis . . . | 14·01 | 5·52 |
| 2. Do. do. . . . | 13·23 | 6·31 |
| 3. Do. do. . . . | 14·25 | 4·84 |
| 4. Do. in massis . . . | 3·37 | 1·27 |
| 5. Do. do. . . . | 3·60 | 2·07 |
| 6. Do. do. . . . | 2·80 | 1·90 |
| 7. Do. do. . . . | 3·00 | 1·86 |
| 8. Do. in tabulis . . . | 1·22 | 0·40 |
| 9. Do. do. . . . | 1·30 | 0·70 |
| 10. Do. do. . . . | 1·80 | 1·30 |
| 11. Do. do. . . . | 1·20 | 0·80 |

Oberdörffer first drew attention to the adulteration of shellac with colophony, and recommended the specific gravity and solubility in ether as a test for this admixture (pure shellac with 25 per cent. of colophony has the sp. gr. 1·120). The natural wax, of which shellac contains about 5 per cent., passes into the ether, a larger percentage of soluble matter indicating colophony. In this connection it should be observed that the percentage of wax fluctuates considerably. Oberdörffer found 5 per cent., Farner 6 per cent.; Benedikt and Ulzer found only 0·5 to 1 per cent. for the wax recovered by means of sodium carbonate; finally, Gascard also obtained 6 per cent. of resin. The specimens examined by the last named and Farner would, according to Oberdörffer's views, be regarded as adulterated with colophony!

Other adulterants are aloe resin, and, according to Mackey, artificial coloration with orpiment (yellow arsenic sulphide) is also practised. These last-named substances remain behind when the substance is treated with alcohol. Colophony may also be detected by the aid of petroleum ether, which dissolves only 3 per cent. of pure shellac, whereas colophony is in some cases entirely soluble, in others only to the extent of about one-half. According to the foregoing data by Hirschsohn, the limit of 3 per cent. does not, however, appear to be tenable, since he found as much as 14 per cent. of substances (dried at 17° C.) soluble in petroleum ether.

In any event, these reports are all so uncertain that we agree with the following opinion expressed by Klar as to the solubility of shellac :—

" In the literature of the subject it is generally prescribed that bleached shellac should not exhibit more than 5 per cent. soluble in ether (colophony test). The author has also

determined the acid and ester values, and found that the wax content exercises a considerable influence on the ethereal extraction value, which, however, as well as the acid and ester value, is apparently of little importance, the values furnished by commercial specimens being so divergent. At present there is no certain, and at the same time simple, method for detecting adulteration in bleached shellac. Its solubility in 96 per cent. alcohol may be influenced partly by the presence of wax, partly by overbleaching, and partly by alterations due to the action of atmospheric air, since, unless stored under water, shellac gradually loses its solubility in alcohol under the influence of the air. None of the attempted filtration or clarification experiments have been successful. Should the bleached shellac—and a small addition of wax would do no harm for polishing purposes—not give a clear solution, Klar recommends a small addition of zinc oxide, which forms a compact substance with the waxy matters if the mixture be left to stand in a warm place, whereby one is enabled in a short time to pour off a clear liquid, though a by no means inconsiderable percentage of shellac is also thrown down."

As regards the acid, ester, and saponification values mentioned by Klar, various figures are met with for these in the literature of the subject.

Williams found (usual method)—

| Shellac. | Ash. % | Loss at 100°. % | Acid Value (direct). | Ester Value. | Saponification Value (hot). | Iodine Value. |
|---|---|---|---|---|---|---|
| Medium button | 1·06 | 0·28 | 63·0 | 140·3 | 203·3 | 24·62 |
| Garnet | 0·72 | 0·37 | 56·0 | 156·6 | 212·6 | 28·70 |
| Fine orange | 1·23 | 0·31 | 64·4 | 142·0 | 206·4 | 17·52 |
| Good 2nd orange | 0·88 | 0·42 | 47·6 | 163·1 | 210·7 | 20·40 |
| Fair do. | 1·01 | 0·63 | 56·0 | 155·4 | 211·4 | 19·81 |
| Inferior do. | 1·41 | 0·94 | 57·4 | 136·7 | 194·1 | 19·05 |

Kremel found by the same method—

| Shellac. | Acid Value. | Ester Value. | Sapon. Value. |
|---|---|---|---|
| White | 73·7 | 102·8 | 176·5 |
| Yellow | 63·5 | 50·2 | 113·7 |
| Lacca in granis (purified by alkali) | — | — | 174·8 |

Von Schmidt and Erban found—

| Shellac. | Acid Value (direct). | Ester Value. | Sapon. Value (hot). | Iodine Value. |
|---|---|---|---|---|
| Brown | 65·1 | 148·2 | 213·3 | 8·3 |
| Orange | 60·0 | 151·6 | 211·6 | — |

Solubility in—

| | |
|---|---|
| Alcohol | soluble. |
| Ether | insoluble. |
| Methyl alcohol | soluble. |
| Amyl alcohol | ,, |
| Benzol | almost insoluble. |
| Petroleum ether | insoluble. |
| Acetone | almost insoluble. |
| Glacial acetic acid | soluble. |
| Chloroform | partly soluble. |
| Carbon di-sulphide | insoluble. |
| Oil of turpentine | almost insoluble. |

Mills and Muter found for shellac, saponification value 230, and bromine value 5·2, and for bleached shellac saponification value 182, and bromine value 4·6.

The solubility in ether and petroleum ether should, according to other authorities, be more correctly stated as "slightly soluble." According to Mauch, both "Lacca in tabulis" and "Lacca depurata in bacillis" are soluble in 80 per cent. chloral hydrate, in which they first swell considerably.

On the solubility of bleached shellac in epi- and di-chlorhydrin (Valenta), see Table in Part I.

D. Hooper gives analyses of the four most important varieties of crude lac, which were found to contain :—

| Variety of Lac | *Kusum.* | *Ficus.* | *Ber.* | *Palas.* |
|---|---|---|---|---|
| Source | *Schleichera trijuga* | | *Zizyphus jujuba.* | *Butea frondosa.* |
| Water | 1·8 | 1·8 | 2·0 | 2·4 |
| Resins | 85·6 | 83·9 | 82·7 | 77·4 |
| Colouring matter | 2·5 | 2·6 | 2·4 | 4·3 |
| Residue | 9·1 | 10·2 | 11·5 | 14·1 |
| Ash | 1·0 | 1·5 | 1·3 | 1·8 |
| | 100·0 | 100·0 | 100·0 | 100·0 |

The average iodine value of these lacs was 11·4 per cent. Two samples of crude lac from the State Gardens at Baroda have been investigated at the Imperial Institute. These were samples of sticklac and seedlac from insects grown on the "rain" tree (*Inga saman* or *Pithecolobium saman*). The twigs of the tree contained 26·8 per cent. of lac and the seed lac had some particles of wood and dust in it.

| | Lac removed from Twigs. | | Seed lac as received. | |
|---|---|---|---|---|
| Moisture | 2·8 | Iodine | 2·7 | Iodine |
| Ash | 1·4 | number of | 2·2 | number of |
| Wax | 9·0 | lac, 5·6; | 6·6 | lac, 4·5; |
| Colouring matter | 7·2 | ditto, after | 12·4 | ditto, after |
| Insoluble matter | 8·1 | removal of | 8·6 | removal of |
| Resin | 71·5 | dust, 4·0 | 67·5 | dust, 3·9 |
| | 100·0 | | 100·0 | |

A. Rudling examined three samples of shellac and gives the following figures :—

| | Water. | Insoluble in Alcohol. | Acid Value. | Saponification Value. | Iodine Value. |
|---|---|---|---|---|---|
| Sticklac | 3·79 | 14·40 | 39·2 | 212·8 | 16·0 |
| Seedlac | 2·63 | 10·69 | 53·0 | 218·4 | 7·5 |
| Buttonlac | 2·00 | 3·10 | 58·8 | 204·4 | 22·2 |

Puran Singh has investigated three specimens of pure lac prepared by himself on a fairly large scale by extracting the crude lacs with wood spirit of 98 per cent. strength. The crude lacs from which these were extracted were obtained

from the Forest Department, Central Provinces, being known as "kusum lac," derived from *Schleichera trijuga*, "palas lac" from *Butea frondosa*, and "block or coagulated" lac, a dark-coloured massive variety which during storage and transport has been agglomerated by pressure. In addition to these a sample of shellac from the Mirzapur factory was included, which was free from colophony but contained a small quantity of the sulphide of arsenic, which is often added to improve the colour. Shellac wax and shellac resin were also examined, the shellac wax being extracted from "kusum" lac by treatment with petroleum spirit boiling at 60°. The melting point of the wax was found to be 58°–59°. The shellac resin was obtained from the residue after the treatment with petroleum spirit, by extracting the colouring matter with hot water, dissolving the resin in alcohol and precipitating with water.

This operation was repeated several times, the resin being finally dried between filter paper in a desiccator. On heating the resin for several hours at 100°–110° resin acid anhydrides were formed and the iodine value was then found to be 10·6.

| | Moisture at 100°. | Insoluble in Alcohol. | Acid Number. | Ester Number. | Saponification Number. | Iodine Number. 18 hours. | Endemann Number. |
|---|---|---|---|---|---|---|---|
| Shellac from "Kusum" lac | 2·7 | 0·7 | 61·1 | 139·9 | 201·0 | 9·6 | 8·4 |
| Shellac from "Palas" lac | 3·8 | 0·8 | 60·8 | 141·6 | 202·4 | 9·3 | 8·0 |
| Shellac from Block lac | 3·9 | 1·1 | 63·1 | 138·5 | 201·6 | 8·2 | 9·2 |
| Mirzapur Factory Shellac | 2·0 | 0·6 | 64·4 | 139·2 | 203·6 | 8·6 | 7·4 |
| Lac Wax . . | — | — | 22·1–24·3 | 57·1–60 | 79·2–85·0 | 8·8 | — |
| Lac Resin (dried) | — | — | 52·1–59·2 | 139·2–141·4 | 193·5–198·4 | 6·8–7·3 | 7·3–8·7 |
| „ „ (melted) | — | — | 54·9 | 135·1 | 190·0 | 5·9 | — |

The Endemann number is the percentage of uncondensable acids, which amount in genuine shellac to 7 or 8 per cent. The method of determination consists in mixing 1·5–2 grms. of the shellac with 3–4 grms. of sand and some concentrated hydrochloric acid. The mass is evaporated to dryness and the residue treated with alcohol, 20 c.c. at a time, the total volume of alcohol used being 150 c.c. The solution is evaporated to dryness and the uncondensed fatty and resin acids weighed. This method has been examined by Langmuir and White, who found it to be untrustworthy.

A very complete series of analyses of shellacs by J. H. Hoseason and O. Klug is reproduced below; the samples examined were the sticklacs known as Baisakhi, collected from April to July; Jetwa, August to October; Katkhi, September to November; and Nagoli, November to March. Nagoli is regarded as the best quality lac, Jetwa, Baisakhi, and Katkhi following in the order given, but the largest crop is the Baisakhi. All the samples of shellac and button lac examined were found to contain arsenic sulphide, but it was not found in the garnet button lac.

STICKLACS

| | Year. | Wax. per cent. | M.P. | Water. Sol. | Ether. Sol. | Ether. Insol. | Residue. | Ash. | Loss and Moisture. | Iodine Value. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Ether. Sol. | Ether. Insol. |
| Baisakhi | 1907 | 5·52 | 83° | 5·33 | 23·5 | 35·25 | 23·63 | 4·32 | 6·77 | 8·9 | 4·63 |
| ,, | 1909 | 5·24 | 80·5° | 5·06 | 26·0 | 37·5 | 23·0 | 6·64 | 3·20 | 7·7 | 7·0 |
| ,, | 1910 | 5·24 | 80° | 2·46 | 28·1 | 49·5 | 10·85 | 7·3 | 3·85 | 7·4 | 2·6 |
| Nagoli . | 1907 | 3·79 | 80° | 3·88 | 26·75 | 42·25 | 18·1 | 2·33 | 5·23 | 5·3 | 4·4 |
| ,, . | 1909 | 3·75 | 80·5° | 4·0 | 27·75 | 41·5 | 19·46 | 6·07 | 3·54 | 9·54 | 3·8 |
| ,, . | 1910 | 3·95 | 80° | 4·03 | 28·82 | 43·36 | 19·33 | 6·34 | 0·51 | 6·8 | 6·3 |
| Katkhi | 1909 | 4·6 | 80° | 6·95 | 24 | 41·25 | 21·2 | 5·13 | 2·0 | 5·8 | 4·0 |
| ,, | 1910 | 5·01 | 80° | 4·42 | 23·5 | 37·0 | 22 | 7·3 | 8·07 | 8·1 | 7·4 |
| Jetwa . | 1909 | 3·6 | 79·5° | 3·69 | 27·75 | 49·75 | 13·5 | 7·8 | 1·71 | 4·5 | 3·6 |
| Assam . | 1910 | 5·2 | 82·5° | 4·45 | 17·01 | 61·0 | 6·7 | 0·55 | 5·64 | 13·9 | 5·3 |
| Siam . | 1910 | 4·59 | 82° | 4·45 | 26·25 | 55·0 | 7·88 | 0·81 | 1·8 | 10·06 | 6·1 |
| Rangoon | 1910 | 5·11 | 82° | 6·47 | 26·25 | 52·25 | 8·0 | 1·1 | 1·92 | 10·0 | 6·1 |

SHELLACS

| | Wax, per cent. | M.P. | Ether. Sol. | Ether. Insol. | Residue. | Loss and Moisture. | Iodine Value. | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Ether. Sol. | Ether. Insol. |
| Button :— | | | | | | | | |
| Dark . . . | 4·75 | 80° | 21·88 | 69·83 | 0·1 | 3·44 | 23·5 | 2·8 |
| Pale . . . | 1·16 | 77° | 30·0 | 65·38 | 0·05 | 3·46 | — | — |
| Pale . . . | 2·4 | — | 43·75 | 50·25 | 0·75 | 3·6 | 20·2 | 2·2 |
| Medium . . . | 5·4 | — | 26·23 | 65·75 | 0·05 | 2·62 | — | — |
| Pale . . . | 6·7 | — | 48·75 | 40·0 | 1·35 | 4·55 | 8·2 | 3·2 |
| Garnet . . . | 2·11 | 77° | 39·63 | 58·1 | *Nil* | 0·16 | — | — |
| Shellacs :— | | | | | | | | |
| Brown, Rangoon . | 3·56 | 82° | 22·0 | 72·75 | 1·10 | 1·69 | 21·6 | 3·4 |
| Dark brown, Baisakhi | 5·55 | — | 30·25 | 61·4 | 1·55 | 2·80 | 10·1 | 2·8 |
| Brown, Katkhi . | 4·7 | 80·5° | 22·5 | 70·0 | 0·70 | 2·80 | — | — |
| Fine orange, Nagoli . | 3·7 | — | 20·25 | 72·25 | 0·90 | 3·72 | 12·8 | 2·1 |

The adulteration of shellac with colophony has been practised for a considerable time, but the various brands on the market are now so well known that it is not difficult to quickly arrive at a conclusion as to their values.

According to E. J. Parry, the most useful indications are the iodine value, the acid value, and the saponification value, the former being the most important; in fact, the purity of a sample of shellac may now be determined by this factor alone. In the past the figures given for shellac have been very variable and somewhat misleading, this being due to the fact that in very few cases were the samples authenticated, the results being obtained with all kinds of commercial samples without any regard being paid to their purity. E. J. Parry, however, examined a large number of samples of shellac which were undoubtedly genuine, and also commercial samples more or less adulterated, and as a result adopted the following figures for shellac and colophony :—

| | Shellac. | Colophony. |
|---|---|---|
| Iodine value | 8–11 | — |
| | Average 9 | Average 125 |
| Acid value | 55–65 | 150–170 |
| | Average 60 | Average 160 |
| Ester value | 155–175 | Seldom reaches 20 |
| | Average 168 | Average 10 |

The iodine values in these cases were obtained by the Hubl method. This method and the standards laid down by Parry are accepted both in London and on the Continent. Many of the earlier estimations of iodine value suffered from the fact that too short a time was allowed for the action, and this remark applies to figures which were given by Parry in earlier communications. The results for both shellac and colophony are now appreciably higher than those quoted when the process was first introduced.

A. C. Langmuir, and later Langmuir and F. S. White, examined a number of shellacs by the Wijs method. They found that samples of shellac received from well-known firms gave iodine values of 13·5–31·4, and the following results for pure shellacs drawn from large lots are quoted.

| | Iodine Value. |
|---|---|
| D.C. | 15·9 |
| Good Ralli | 16·0 |
| Good T.N. | 17·7 |
| Good Button (year 1897) | 15·8 |

Since many other samples in which no evidence of resin could be detected yielded iodine values of 18 or less, this figure was taken for shellac for purposes of calculation.

The iodine value of samples of rosin of American origin varied between 175·7 and 262·5, but the average figure for a number of light coloured rosins was 228, which figure was taken as representing a fair average for rosin.

The method of estimating the iodine value with Wijs solution was investigated by a committee of the American Chemical Society, who reported in favour of it and adopted the figures for shellac and colophony given by Langmuir, so that it is now the official method in use in the United States.

Parry states that he has found some samples of shellac to contain 20–35 per cent. of rosin, and a few even over 40 per cent. Orange shellac containing up to 3 per cent. of colophony would pass as genuine. Garnet and button lacs are, as is now well known, rarely, if ever, free from rosin.

There are a few qualitative and other tests for rosin in shellac which merit attention here, although they are not any improvement on the tests already given.

E. J. Parry states that the Storch-Morawski test will detect rosin when present to the extent of 8 per cent. He also mentions the fact that although ether and petroleum ether have often been recommended for extracting and estimating the rosin, unless the material has been added in the powdered state, which is very unlikely, these have very little action, and they fail to extract nearly all the rosin from a mixture, even when it is finely powdered. The same author proposes the following simple test for colophony. The powdered sample is triturated from time to time with petroleum ether, the latter is then filtered off and shaken with water containing a small quantity of cupric acetate in solution, when if colophony is present the ether assumes a more or less pronounced green colour. Although this test works satisfactorily with mixtures containing 30–40 per cent. of colophony, it sometimes fails to give any indication when even as much as 8 or 10 per cent. of rosin is present; in such cases it is better to dissolve the shellac in a little alcohol, pour the solution into water, which precipitates

the material in a finely divided condition, and after drying, this is tested in the manner indicated above.

Another test recommended by the same author is based on the Gladding and Twitchell methods for separating fatty and rosin acids: 0·5 grm. of the sample is dissolved in the minimum quantity of alcohol, phenol-phthalein is added and the liquid carefully neutralised with potassium hydrate; it is then poured into a separator containing 100 c.c. of water, 0·5 grm. of silver nitrate dissolved in a little water is added and the mixture shaken. The liquid is shaken twice with ether, which dissolves the silver salts of the rosin acids; it is filtered into a second separator, washed several times with water and shaken with dilute hydrochloric acid, which liberates the rosin acids. The ether solution is washed several times with water to remove free hydrochloric acid and also the suspended silver chloride, and after filtration the ether is evaporated off and the residue dried at 100° and weighed. There are slight errors in this process, nevertheless in test analyses the results approximated nearly to the truth, but are usually 2 or 3 per cent. too high.

F. Ulzer and R. Defris found that in Gladding's process the resin acids of shellac did not behave the same as those of ordinary rosin. Thus a dark-coloured sample containing 0·05 per cent. of unsaponifiable matter and having acid number 65·43 and saponification number 204·78 yielded only 13·76 per cent. of resin acids. The resin acids of shellac form silver salts which are mainly insoluble in ether, while the silver salts of the acids from colophony are soluble. A mixture of 49 parts of acids from the above shellac with 50 parts of colophony containing 12·9 per cent. of unsaponifiable matter yielded 48·64 per cent. of resin acids. A commercial lac containing colophony yielded only 63·7 per cent. of resin acids.

By Twitchell's method a dark-coloured sample of shellac yielded 66·56 per cent. of resin acids, and the petroleum ether was found to contain an ester, which on drying formed a yellow transparent resinous material, with saponification value 199·5 and no acid value. An orange shellac with acid value 53·05 and saponification value 201 yielded 72·89 per cent. of resin acids. From these results it is evident that the acids of shellac behave to some extent like fatty acids.

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## 37. Storax.

*Balsamum Styracis* (officinal in Germ. Pharm. III.).

**Origin and Habitat.**—*Liquidamber orientalis*, M. (Hamamelideæ). Asia Minor.

**Chemical Constituents.**—Styrol ($C_6H_5.CH = CH_2$), Cinnamic acid ($C_6H_5.C.H.CH.COOH$), Styracin or Cinnamic cinnamester ($C_9H_7O_2.C_9H_9$, M.P. 38°), Cinnamic phenylpropyl ester ($C_6H_5.CH = CHCOOCH_2CHC_6H_5$), Cinnamic ethyl ester ($C_9H_7O_2.C_2H_5$), vanillin (K. Dieterich), ethyl vanillin (von Miller), $\alpha$- and $\beta$-storesin ($C_{35}H_{55}(OH)_3$), amorphous resin, traces of benzoic acid, and cinnamic storesin ester (von Miller). The yield of cinnamic acid varies from 6–12 per cent., but according to Löwe as much as 23 per cent. may be present.

There is also present, according to Simon, a hydrocarbon

—phenylethylene—($C_8H_8$ or $C_6H_5.CH = CH_2$), boiling point 146° and sp. gr. 0·924, while Van t'Hoff has separated about 0·4 per cent. of a sweet-smelling lævorotatory oil of the formula $C_{10}H_{16}O$.

Tschirch and L. v. Itallie found in storax :—free cinnamic acid, vanillin, styrol, styracin, the ethyl and propyl esters of cinnamic acid, and storesinol, partly in the free state and partly combined as a cinnamic ester.

American storax from *Liquidamber styraciflua* contains styrol, styracin, oxygenous oil, cinnamic phenylpropyl ester, and storesin (von Miller).

**General Properties and Commercial Varieties.**—Ordinary storax, from Asia Minor, is a turbid, hydrated, viscid, sticky, grey balsam, of spicy, irritant flavour, possessing an odour like benzoin. It is partly soluble in benzol and petroleum ether, and almost completely so in ether and alcohol. Under the microscope it exhibits crystals. Formerly the name Storax was also applied to the resin from *Styrax officinalis*, for which reason this tree is still often—though erroneously—classed as a storax producer (see below, under *S. calamitus*). " Purified storax " (by treatment with ether) is turbid, thickish, sometimes crystalline, light brown; that purified with benzol, benzine, or alcohol is of a faint dark brown colour and thick consistence. A so-called strained (" koliert ") storax is a crude product, freed from the coarser impurities and water, and is intermediate between the quite crude and the purified article.

A *Styrax cum oleo olivarum* is used as a solution or emulsion in pharmacy for convenience in dispensing, and is favoured by the medical profession, since it is easy to triturate and manipulate for use in cases of itch, etc.

American storax, known in America as " sweet gum," is derived from *Liquidamber styraciflua ;* it is mostly used for

chewing. According to Guibourt, this balsam is identical with (white) Peruvian balsam (*q. v.*). A storax balsam which, however, is used solely in the country as a remedy for Psoriasis, is derived from *Microstemon* (Anacardiaceæ). The residual expressed bark left from the preparation of storax is used as a fumigant, under the name *Styrax calamitus*; and a mixture of storax and sawdust is also sold under the same title, as was also formerly the resin from *S. officinalis.*

The origin, derivation, and pharmacognosis of the varieties of storax have been described by Mœller (*Ap. Ztg.*, 1894, p. 752; 1896, p. 207; 1897, p. 596).

**Adulterants.**—Turpentine, colophony, castor oil, olive oil, and fatty oils in general, vegetable impurities, and water. At one time labdanum also was used to adulterate storax.

**Analysis.**—Many investigations have been undertaken on storax, particularly with regard to its purification and the preparation of a uniform product suitable for medicino-pharmaceutical purposes. The irregularity and adulteration of storax have also been referred to on many occasions; at times it would seem that artificial products alone were to be found in commerce. Recently the author examined pure authenticated specimens of storax taken direct from the parent tree, and laid the first foundations of the scientific testing and valuation of this product. As in the case of Peruvian balsam, these researches showed that the commercial varieties—a large number of which were examined—were quite different in composition to the pure natural drug. This—which was also referred to by earlier authorities, such as Mylius, Gehe & Co., and others—seems still to be the case, and, apparently, perfectly pure commercial storax is practically non-existent.

The various kinds and forms of storax will now be dealt with in detail *seriatim.*

**I. Crude Storax** (*Styrax liquidus crudus*).—The numerous estimations of acid, ester, saponification, and iodine values, and the results obtained, are of merely relative value in the examination of storax, because for the most part the determinations were made with alcoholic extracts, and not with the natural storax. The disadvantages of using only portions of a drug, instead of the crude product, have already been fully dealt with in these pages, and therefore need only be mentioned here. It is not clear from the reports of Kremel, Beckurts and Brüche what methods these authors employed; we must therefore leave it an open question whether they examined an extract or the crude product. At all events, E. Dieterich, Evers, and others used extracts. The present author has recently worked out a method which is suitable for direct application to crude storax, and therefore enables reliable conclusions to be formed with regard to the natural drug.

Just as attention was directed by Gehe & Co., Mylius, and others to the existence of adulteration, so various proposals have been made for detecting the same. Thus, E. Dieterich proposed to employ the acid value (direct) for this purpose, seeing that natural turpentine (not Venice turpentine) and colophony give higher acid values than storax. Similarly, Beckurts and Brüche advocated the ether, saponification, and iodine values for detecting adulteration; and Evers believed that the iodine value, and sp. gr. in particular, were worthy of recommendation.

Hirschsohn examined several samples to determine the amounts (dried at 17° and 120° C.) taken up by petroleum ether, and found—

| | Per cent. soluble— | |
|---|---|---|
| | Dried at 17° C. | at 120° C. |
| (1) | 59·12 | 52·09 |
| (2) | 43·30 | 32·82 |
| (3) | 54·76 | 47·98 |

After being heated to 120° C. the residues were colourless, almost inodorous, oily, sometimes setting to a crystalline mass.

According to Hager, the adulteration of storax with turpentine can be detected by petroleum ether. C. Ahrens gives the amount soluble in petroleum ether as lying between 37·6 and 56. The acid value of this extract varies from 33·1 to 62·9 and the cold saponification value 191·3 and 203·3. For the detection of castor or olive oil he recommends the determination of the iodine value.

A. Kremel found—

| | |
|---|---|
| Acid value (direct) | 47·6 |
| Ester value | 31·9 |
| Saponification value (hot) | 79·5 |

by the usual method.

Von Schmidt and Erban also found by the same method—

| | |
|---|---|
| Acid value (direct) | 179·5–130·6 |
| Ester value | 68·8– 75·0 |
| Saponification value (hot) | 198·3–205·6 |
| Iodine value | 64·7 |

Solubility in—

| | | | |
|---|---|---|---|
| Alcohol | partly soluble. | Petroleum ether | insoluble. |
| Ether | ,, | Acetone | partly sol. |
| Methyl alcohol | ,, | Glacial acetic acid | ,, |
| Amyl | ,, | Chloroform | ,, |
| Benzol | ,, | Car. disulphide | slightly sol. |

Oil of turpentine . . . . partly soluble.

Using extracts of the drug, E. Dieterich obtained the following figures :—

| | |
|---|---|
| Acid value (direct) | 37·19– 96·65 |
| Ester value | 74·60–168·00 |
| Saponification value (hot) | 134·60–249·00 |
| Ash | 0·07– 1·20 per cent. |
| Loss at 100° C. | 10·25– 40·15 ,, |

Solubility in—

| | |
|---|---|
| Alcohol (90 per cent.) | 56·14–84·00 per cent. |
| Acetic ether | 69·40–73·60 „ |
| Chloroform | 69·20–72·60 „ |
| Ether | 65·80–82·80 „ |
| Benzol | 64·80–74·80 „ |
| Oil of turpentine | 54·40–57·80 „ |
| Carbon di-sulphide | 62·30–67·80 „ |
| Petroleum ether | 15·00–19·40 „ |

The acid, ester, and saponification values were determined with an alcoholic solution of the alcoholic extract by the same method as employed by Kremel.

Beckurts and Brüche found—

| No. | Sp. gr. | Solubility in equal volume of Alcohol. | Acid Value (direct). | Ester Value. | Saponification Value (hot). |
|---|---|---|---|---|---|
| 1. | 1·116 | 61 per cent. | 80 | 113 | 193 |
| 2. | 1·121 | 72 „ | 91 | 120 | 214 |
| 3. | 1·113 | 62 „ | 68 | 112 | 180 |
| 4. | 1·113 | 66 „ | 69 | 153 | 222 |
| 5. | 1·120 | 71 „ | 75 | 130 | 205 |
| 6. | 1·118 | 64 „ | 93 | 115 | 208 |

The acid, ester, and saponification values were found by the usual method, but it is not clear whether the unfiltered solution (*i. e.* the crude product) or the alcoholic solution of an extract was used.

The author has obtained the following figures, the constants being furnished by the extract :—

| | I. | | II. | |
|---|---|---|---|---|
| Loss at 110° C. | 19·43 per cent. | | 24·05 per cent. | |
| Ash | 0·35 „ | | 0·71 „ | |
| Soluble in alcohol | 77·43 „ | | 73·87 „ | |
| Insoluble | 4·23 „ | | 3·36 „ | |
| Acid value (direct) | 57·51 | 57·90 | 59·29 | 59·41 |

Evers says—

"The directions of the (German) Pharmacopœia are altogether insufficient, since a storax adulterated with 10–20 per cent. of turpentine will pass the Pharmacopœia test completely. The estimation of the specific gravity—especially at 100° C., in a manner similar to that of E. König for testing butter fat—is of the greatest value for detecting adulteration; all extraneous admixtures, such as turpentine, colophony, fats, and oils, reducing the figure. The test should be performed with purified storax, which has been heated in a water oven (at 100° C.) for about three hours, in order to drive off any remaining alcohol.[1] The reading is not taken until the storax has attained the temperature of 100° throughout the entire mass. To facilitate this, it is advisable to carefully raise and lower the spindle several times in the storax; this is calibrated for 100° C., and provided with a scale for sp. grs. between 1·095 and 1·120. The specific gravity of purified storax is 1·109–1·114; that of the crude product, merely deprived of water and clarified by subsidence in a warm place, being somewhat higher. An addition of 10 per cent. of turpentine reduces the specific gravity considerably. Purified storax, showing a specific gravity of less than 1·107 at 100° C., should be regarded with suspicion at least; and if the specific gravity be lower than 1·104, the goods should be rejected as adulterated."

In this connection, it may be remarked that these values do not agree at all well with those obtained by Beckurts and Brüche. The examination of a large number of commercial varieties would indicate that no reliable conclusions can be based on the specific gravity of storax as a guide to purity,

[1] No account is taken here of the volatile constituents. Can the final product still be regarded as storax?—K. D.

in view of the original percentage of water in the substance or the saline content of that water.

Evers carried out further researches, and recommended the iodine value for detecting adulteration. For purified dehydrated storax he found—

| | | | | | |
|---|---|---|---|---|---|
| From extract | Sp. gr. . . | 1·119 | 1·117 | 1·119 | 1·120 |
| | Acid value (direct) | 52·2 | 56·7 | — | — |
| | Ester value . . | 184·2 | 173·5 | — | — |
| | Sapon. value (hot). | 236·4 | 230·2 | — | — |

On this point the author has already expressed himself as follows :—

" Evers has recently expressed himself in favour of the iodine value determination for storax. However, as he did not succeed in detecting adulterations by the iodine value, only moderate importance can be attached to this constant, since the acid and saponification values suffice for identification. As Evers admits, the titration in the iodine value estimation for storax is occasionally very difficult, owing to the formation of dark precipitates, which ball together and occlude iodine.

" Moreover, Evers examined only two adulterated specimens (containing castor oil and turpentine), whereas other adulterations, such as with benzol, Tolu balsam, colophony, rosin oils, etc., ought also to be tested. The advocated iodine value, however, as the figures show, did not prove suitable for detecting the aforesaid adulterations; and, as a means of identification, it is scarcely necessary, since the acid, ester, and saponification values are sufficient.

" It must also be admitted that, when an alcoholic extract is used, the liquids are dark coloured, not only for the iodine value, but also for the acid, ester, and saponification

values, are very difficult to titrate, and, above all, the detection of the colour-change is very difficult."

In order to obtain values which shall correspond in all cases to the unaltered drug, and afford a basis for valuing the commercial product, the author recently examined some perfectly pure specimens of storax which were authentic, and taken direct from the parent tree; at the same time various samples of the commercial product were also tested for the sake of comparison.

The method employed by the author had mainly in view the utilisation of an unfiltered alcoholic solution of crude storax, in place of the extracts used hitherto, and the obtainment of a light coloured, easily titrated saponification liquid by the cold process. The method was based on the results of numerous preliminary experiments, which need not be here detailed.

The following results were obtained in the comparative experiments between the crude products and the extract :—

I. The original drug gave—

| | | |
|---|---|---|
| Acid value (direct) . . . | 49·045 | 50·053 |
| Saponification value (cold) . . | 156·726 | 157·460 |

II. Alcoholic extract.—The values refer to 1 grm. of extract, not 1 grm. of crude product—

| | | |
|---|---|---|
| Acid value (direct) . . . . | 55·040 | 56·297 |
| Saponification value (cold) . . | 194·300 | 194·565 |

III. Alcoholic extract.—The values are calculated to 1 grm. of crude product—

| | | |
|---|---|---|
| Acid value (direct) . . . | 40·208 | 40·873 |
| Saponification value (cold) . . | 141·913 | 142·122 |

From these experiments it is evident that—

(*a*) The values obtained from, and calculated on the extract are much higher than those from the crude product, since they naturally correspond to more than 1 grm. of the initial material. The values so obtained, therefore, cannot be considered as on a par with the saponification values of the crude product, or serve as a criterion for the latter.

(*b*) The values obtained with the extract, and then calculated to 1 grm. of crude product, are much lower than those from the crude drug itself, owing to the loss of volatile matter during the preparation of the extract.

(*c*) As a general rule, none of the values furnished by the extract agree with those yielded by the crude drug, nor can they serve as a basis for conclusions based upon the latter; indeed, the figures obtained from the crude product are alone suitable as a guide to the valuation of the same.

The author's method is as follows :—

(*a*) *Loss at* 100° *C.*—Two grms. of storax are dried at 100° C. in the water oven until of constant weight.

(*b*) *Determining the amount soluble in alcohol.*—Ten grms. of storax are weighed into a 200 c.c. beaker and dissolved by warming in 100 c.c. of 96 per cent. alcohol, the solution is passed through a dry, tared filter into a tared porcelain basin, the beaker and filter being washed with 50 c.c. of hot alcohol. The filtrate is concentrated by evaporation, and the residue dried at 100° C. till constant. It is advisable to weigh along with the basin a small glass rod, which serves to stir the resinous residue during drying. To prevent the troublesome creeping which occurs during the evaporation of resin solutions, it is advisable to float the porcelain basin in a larger basin of water, instead of placing it direct on the water or steam bath. The resin solution will then creep only

to the same height as the level of the water in the outer basin.

(*c*) *Determining the amount insoluble in alcohol.*—The insoluble residue from the preceding estimation is weighed and calculated to percentage.

(*d*) *Ash.*—The dried storax from *a* is incinerated and calcined until constant.

(*e*) *Acid value* (direct).—About 1 grm. of storax is dissolved in 100 c.c. of 96 per cent. alcohol, without heat, and titrated with alcoholic $\frac{n}{2}$ caustic potash and phenolphthalein until the colour changes to red. The number of c.c. of KHO consumed, multiplied by 28·08, gives the acid value.

(*f*) *Saponification value* (cold).—About 1 grm. of storax is treated with 20 c.c. alcoholic $\frac{n}{2}$ potash and 50 c.c. of benzine (sp. gr. 0·700) in a 1 litre flask, fitted with a ground stopper. After standing for twenty-four hours at room temperature, the contents are titrated back with $\frac{n}{2}$ sulphuric acid, using phenolphthalein as indicator, without addition of water. The volume (c.c.) of combined $\frac{n}{2}$ potash, multiplied by 28·08, gives the saponification value.

(*g*) The *ester value* is found by subtracting the acid value from the saponification value.

It should be noted that the storax must be freed from any mechanically adherent water before it is submitted to analysis; the water that is to some extent combined in the form of emulsion, however, being included for the determination. Further artificial addition of water, beyond the natural quantity that is left in the boiling, can only be incorporated by proper mixing and emulsification, and not by mere contact as a supernatant stratum. The latter must be regarded as adulteration.

As it is difficult to weigh out 1 grm. with accuracy in the case of storax, and weighing into a narrow-necked

flask is also troublesome, the best method is to take up the drug on the tip of a small weighed glass rod, the whole being then placed together in the flask.

With authentically pure varieties of storax the author obtained the following values :—

| | | |
|---|---|---|
| Moisture . . . | 26·21–40·97 % | |
| | Calculated to natural drug containing original moisture. | Calculated to dry drug. |
| Ash . . . . | 0·5 – 0·92% | 0·74– 1·25% |
| Soluble in alcohol . | 57·14– 65·49% | 88·75–100·20% |
| Insoluble in alcohol . | 1·45– 2·61% | 1·97– 3·85% |
| Acid value (direct) . | 59·38– 70·70 | 87·62– 95·81 |
| Ester value . . | 35·42– 74·43 | 49·84–109·83 |
| Sapon. value (cold) . | 104·67–135·36 | 145·62–199·74 |

The numerous commercial varieties examined gave the following values :—

| | | |
|---|---|---|
| Moisture . . . | 19·58–31·95 % | |
| | Calculated to natural drug. | Calculated to dry drug. |
| Ash . . . . | 0·24– 3·64% | 0·57– 4·75% |
| Soluble in alcohol . | 64·90– 77·17% | 89·62– 99·63% |
| Insoluble in alcohol . | 1·66– 7·33% | 2·45– 9·56% |
| Acid value (direct) . | 38·22– 72·29 | 54·96–106·23 |
| Ester value . . | 47·81–110·03 | 72·82–142·47 |
| Sapon. value (cold) . | 111·89–187·76 | 170·41–233·40 |

On comparing these two sets of figures it will be seen that—as in the case of Peruvian balsam—nearly all the commercial kinds are adulterated, impure, or of low quality. To apply the standards obtained by the pure drug to the commercial kinds would practically boycott nearly all the latter. In order to obtain some idea what limits of requirement to prescribe, the author added various materials to pure specimens of the drug and examined the products, the results being given in the subjoined table :—

**Adulteration of Styrax liquidus crudus.**

a = calculated to natural drug. b = calculated to dried drug.

| Authentically pure *Styrax liquidus crudus.* | Moisture % | Ash % | | Soluble in Alcohol % | | Insoluble in Alcohol % | | Acid Value (direct). | | Ester Value. | | Saponification Value (cold). | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | a | b | a | b | a | b | a | b | a | b | a | b |
| + 20 % of Olive oil | 33·73 | 0·62 | 0·94 | 63·87 | 96·38 | 1·63 | 2·46 | 53·65<br>58·55 | 80·96<br>88·35 | 72·98<br>68·52 | 110·12<br>103·39 | 126·63<br>127·07 | 191·08<br>191·74 |
| + 30 % of Olive oil | 28·22 | 0·47 | 0·65 | 70·59 | 98·34 | 1·25 | 1·74 | 53·08<br>55·73 | 73·95<br>77·64 | 78·34<br>80·87 | 109·14<br>112·68 | 131·42<br>136·60 | 183·09<br>190·32 |
| + 20 % of Castor (ricinus) oil | 33·96 | 0·51 | 0·77 | 64·72 | 98·00 | 1·32 | 2·00 | 57·21<br>58·41 | 86·63<br>88·45 | 66·84<br>66·78 | 101·21<br>101·12 | 124·05<br>125·19 | 187·84<br>189·57 |
| + 30 % of Castor (ricinus) oil | 29·30 | 0·33 | 0·47 | 69·65 | 98·52 | 0·94 | 1·32 | 51·31<br>52·36 | 72·57<br>74·06 | 79·88<br>78·95 | 112·98<br>111·67 | 131·19<br>131·31 | 185·55<br>185·73 |
| + 20 % of ordinary Turpentine | 39·56 | 0·61 | 1·01 | 59·30 | 98·11 | 1·17 | 1·94 | 78·40<br>79·62 | 129·72<br>131·73 | 29·53<br>37·16 | 48·86<br>61·48 | 107·93<br>116·78 | 178·58<br>193·21 |
| + 30 % of ordinary Turpentine | 34·62 | 0·53 | 0·81 | 63·36 | 96·91 | 1·10 | 1·68 | 84·04<br>84·43 | 128·54<br>129·14 | 23·01<br>23·01 | 35·20<br>35·20 | 107·05<br>107·44 | 163·74<br>164·34 |

These figures show that the added extraneous substances have all modified the values of normal storax, the fatty oils reducing the acid value, but raising the ester and saponification values; whilst turpentine, on the other hand, depresses the ester value, and, as already shown by E. Dieterich, considerably raises the acid and saponification values. Nothing abnormal is discernible in the ester value; consequently the acid, ester, and saponification values, and, in addition, the determination of the percentage soluble in alcohol, are all factors capable of affording useful indications as to the quality of storax.

On the basis of the results furnished by the pure specimens, and in the above experiments with adulterants, the author has proposed the following limits, which, while not being too stringent, are so drawn as to permit the detection of any considerable degree of adulteration :—

1. Moisture : not to exceed 30 per cent.
2. Ash : not more than 1 per cent.
3. Soluble in alcohol : not below 60 per cent. (the former limit of 70 per cent. appears too high).
4. Insoluble in alcohol : not to exceed 3 per cent.
5. Acid value (direct) . . 55– 75
6. Ester value . . . 35– 75
7. Saponification value (cold) . 100–140

(5, 6, 7: in round numbers.)

The opinion may, however, be expressed that further experience is necessary to show whether these values, especially the three last-named constants, are justified.

Gregor and Bamberger gave the following methoxyl values :—

| | I. | II. |
|---|---|---|
| Gregor . . . . . | 4·5 | 3·6 |
| Bamberger . . . . | 0·0 | — |

**II. Purified Storax.**—A considerable amount has been written on the methods of purifying storax, some authors

recommending alcohol, benzol, benzine, or petroleum ether, whilst others advocate ether. Mylius, in particular, who has performed useful work in this connection, advises the use of petroleum ether which does not dissolve the inactive resin. Nevertheless, he further states that the mixture of oil and storax should be prepared with castor (ricinus) oil, and not olive oil, since the latter precipitates the resin, which is an active ingredient in the liniment. Schlickum and E. Dieterich prefer the use of ether, which, in the author's opinion, also, is the best for the purpose, since it dissolves a large quantity of storax, and is, moreover, so readily removed by evaporation that the loss of the volatile constituents of the storax is reduced to a minimum. Next in value to this solvent is alcohol, then follow petroleum ether and benzine, benzol being the least useful.

The author experimented in this connection with the previously mentioned authentically pure samples of storax, and found that alcohol dissolved 65 per cent., ether 69·5 per cent., benzine 56·5 per cent., and benzol 64·3 per cent.

The product, purified by solution in alcohol, was dark brown, almost perfectly clear; that with ether, pale, like an emulsion; that with benzine, light yellow and clear; and that with benzol, brown and clear. The analytical values, given below, also show that the ether method is the only correct one, since it furnishes a product most nearly approximating to the original material.

With regard to the purification of storax, or the preparation of *Styrax liquidus depuratus*, D. A. III., Krüer has made certain proposals, which are mentioned here, not because they bring about any improvement, but as a warning, since such a method would remove some of the essential constituents of the storax. He proposes to boil the drug over an open fire to drive off water, after which it is strained, and

so purified. It is scarcely necessary to point out that to boil a resin like storax, which contains so large a percentage of volatile and easily decomposable constituents, is altogether inadmissible, in view of its result.

Though the method may be convenient, it certainly cannot be characterised as *lege artis*. A product of such a " secondary " nature as storax, which has already undergone modification and become different from the natural product, would be altogether altered by such a method of treatment.

Evers gives the following values for purified storax :—

| | Sp. gr. at 100° C. | Acid Value (direct). | Sapon. Value (hot). | Ester Value. |
|---|---|---|---|---|
| | 1·109 | 55·7 | 216·0 | 160·3 |
| | 1·109 | 67·0 | 216·0 | 149·0 |
| | 1·114 | 61·2 | 211·5 | 150·3 |
| | 1·110 | 56·0 | 217·9 | 161·9 |
| | 1·110 | 56·3 | 222·3 | 166·0 |
| | 1·111 | 62·8 | 221·3 | 158·5 |
| | 1·113 | 60·2 | 221·1 | 160·9 |
| | 1·110 | 58·0 | 218·6 | 160·6 |
| | 1·109 | 57·4 | 218·9 | 161·5 |
| | 1·113 | 59·0 | 216·6 | 157·6 |
| | 1·111 | 56·1 | 221·2 | 165·1 |
| Average | 1·111 | 59·1 | 218·3 | 159·2 |
| Limits | 1·109–1·114 | 56·0–67·0 | 211·5–222·3 | 149·0–166·0 |

Kremel found—

| | |
|---|---|
| Acid value (direct) | 61·0 |
| Ester value | 76·0 |
| Saponification value (hot) | 137·0 |

These values are much lower than those of Evers, though obtained by the same method.

E. Dieterich found—

| | |
|---|---|
| Acid value (direct) | 56·94– 84·00 |
| Ester value | 105·77–173·00 |
| Saponification value (hot) | 178·45–257·00 |
| Ash | 0·00– 0·14 % |
| Loss at 100° C. | 5·06– 12·63 % |
| Soluble in petroleum ether | 37·54– 58·96 % |
| Insoluble do. do. | 37·00– 63·15 % |

Solubility in—

| | |
|---|---|
| Alcohol (90 per cent.) | almost to completely soluble. |
| Ether | 93·14 per cent. to completely soluble. |
| Chloroform | almost to completely soluble. |
| Acetic ether | completely soluble. |
| Benzol | 95·75 per cent. to almost completely soluble. |
| Petroleum ether | 38·18–62·18 % soluble. |
| Oil of turpentine | 81·80–99·55 % soluble. |
| Carbon di-sulphide | 86·80–93·39 % soluble. |

As previously stated, the author has also examined purified storax and obtained standard values for the authentically pure kinds in the purified condition. The method used was that already described under *Styrax crudus*.

The following limits were obtained with authentically pure, unadulterated storax, ether being used to purify the preparations :—

Water 15 %

| | Calculated to Material— Undried. | Dried. |
|---|---|---|
| Ash | 0·03 % | 0·04 % |
| Acid value (direct) | 85·97– 88·51 | 101·73–104·73 |
| Ester value | 52·11– 52·26 | 61·66– 61·84 |
| Sapon. value (cold) | 138·23–140·62 | 163·57–166·39 |

Using the same method a number of commercial varieties gave the following values :—

| | | Calculated to Material— | |
|---|---|---|---|
| | | Undried. | Dried. |
| Water . . . . | 5·91– 10·35 % | | |
| Ash . . . . | 0·01– 0·47 % | 0·01– 0·52 % | |
| Acid value (direct) . | 59·69– 95·06 | 63·45–116·15 | |
| Ester value . . | 54·07–129·44 | 66·08–137·27 | |
| Sapon. value (cold) . | 148·16–192·61 | 181·05–208·66 | |

As in the case of the crude products, considerable divergencies exist between the normal samples and the purified commercial grades, a matter of small wonder in view of the differences in the composition of the initial materials.

On the basis of the foregoing experience, the author proposes the following limits for the different constants :—

Water : maximum 15 per cent. (the former limit of 8 per cent. appears to be too low).

Ash : „ 0·5 „

| | |
|---|---|
| Acid value (direct) . . . | 70–90 |
| Ester value . . . . | 50–120 |
| Saponification value (cold) . . | 135–180 |

} in round numbers.

It must be left to the future and to wider experience to determine whether these limits are to stand. It is the author's opinion that, in comparison with normal storax, they are too wide, although it should be borne in mind that if the requirements were made too stringent nearly all the purified commercial grades would fail to pass.

**III. Styrax crudus colatus.**—Under this name there exists in commerce a product which has been freed, as far as possible, from dirt, wood, resin, and water by straining. As the constants have been ascertained, they may be reproduced here.

E. Dieterich found :—

| | | |
|---|---|---|
| From extract | Acid value (direct) . . . | 63·03– 88·04 |
| | Ester value . . . . . | 139·02–140·99 |
| | Saponification value (hot) . . | 203·13–227·16 |

The author found, for *S. crudus colatus* prepared from commercial varieties—

| | |
|---|---|
| Loss at 100° C. . . . . | 27·00–34·75 per cent. |
| Ash . . . . . | 0·00– 1·02 ,, |
| Soluble in alcohol . . . | 66·4 ,, |
| Insoluble in alcohol . . . | 2·1 ,, |

A preparation of this kind from the authentically pure specimens of storax already mentioned, was also prepared and examined in an unextracted condition by the method detailed under *S. liquidus crudus*, with the following results:—

Water . . . 37·83 %

| | Calculated to Material— Undried. | Dried. |
|---|---|---|
| Ash . . . | 0·57 % | 0·92 % |
| Soluble in alcohol . | 60·83 % | 97·84 % |
| Insoluble do. . | 1·19 % | 1·94 % |
| Acid value (direct) | 70·18– 70·89 | 110·03–112·88 |
| Ester value . . | 35·91– 39·74 | 57·76– 63·49 |
| Sapon. value (hot) | 106·09–110·36 | 170·64–177·52 |

With regard to the method of heating employed in the preparation of *S. crudus colatus*, the remarks relating to Krüer's method of purifying storax also apply.

(For a discussion on the German Pharmacopœia tests for storax, see *Ph. C.*, 1898, No. 20.)

C. A. Hill and T. T. Cocking state that cinnamic acid is not completely extracted even when the storax is shaken five times with hot water, and that it cannot be dried to constant weight at 100° C., hence they prefer to extract with boiling water under an inverted condenser, and either

to dry in vacuo over sulphuric acid or dissolve the acid in alcohol and titrate with alkali. A sample of storax, which by Umney's method yielded 28 per cent. of cinnamic acid, was found by the modified process to contain 30·68 per cent.

L. van Itallie and H. J. Lemkes state that the cinnamic acid in storax occurs both in the free state and as cinnamyl, phenylpropyl, ethyl, and ricinoleic esters. The amount of free cinnamic acid cannot be calculated from the acid value, since insoluble acids are also included. They propose the following method of estimating the total cinnamic acid: 1 grm. of the sample is heated with 2 c.c. of $\frac{n}{2}$ alcoholic potassium hydroxide under an inverted condenser. The solution is evaporated to dryness and 25 c.c. of water added to the residue to dissolve it, this is shaken with 20 c.c. of ether, and separated, the ether being washed twice with 5 c.c. of water. The united aqueous solutions are made up to 950 c.c. and shaken with 10 c.c. of dilute sulphuric acid, the whole then being made up to 1000 c.c. and filtered: 100 c.c. of the filtrate is treated with 10 c.c. of $\frac{n}{10}$ potassium bromate solution, 1 grm. of potassium bromide and 5 c.c. of sulphuric acid; after standing 15 minutes potassium iodide solution is added, and, after 5 minutes, the liberated iodine is titrated with $\frac{n}{10}$ thiosulphate solution. 1 c.c. of $\frac{n}{10}$ $KBrO_3$ solution equals ·0074 grm. of cinnamic acid.

According to Evans', the results obtained by this method are 2–3 per cent. higher than those by the method of Hill and Cocking. Not only is the full amount of cinnamic acid obtained, but any resin acids present are eliminated by solution in the ether.

The adulteration of storax with pine resins and fatty matter may be detected by the amount soluble in petroleum ether and determination of the acid value of the soluble

portion. Thus Evans' found the amount soluble in presumably pure commercial samples of storax to be 3·5–12 per cent. and its acid value 3–40, whereas with adulterated samples the petroleum ether extract amounted to 46–80 per cent., and its acid value 97–114·8.

J. C. Umney calls attention to the fact that storax as imported direct from Asia Minor has the same fragrance as in former years, but that brought through certain ports, particularly Trieste and Marseilles, is now quite different, the extraction of certain constituents upon which the value of the balsam depends being largely practised with the consequent production of a poorer article. To illustrate this he gives the following table of analyses, the samples having been obtained from dealers and not producers :—

| | Acid Value. | Ester Value. | Cinnamic Acid, free and combined, per cent. |
|---|---|---|---|
| 1907 | 68·9 | 111·9 | 19·0 |
| 1907 | 67·1 | 120·9 | 15·2 |
| 1908 | 96·4 | 94·0 | 14·1 |
| 1909 | 95·9 | 65·4 | 11·6 |
| 1909 | 111·6 | 63·0 | 11·7 |
| 1910 | 101·5 | 92·4 | 9·3 |
| 1910 | 93·7 | 84·4 | 8·2 |
| 1910 | 97·1 | 90·2 | 8·3 |
| 1910 | 99·4 | 30·3 | 7·6 |
| 1911 | 110·3 | 82·8 | 7·5 |
| 1911 | 107·0 | 81·8 | 5·6 |
| 1911 | 99·7 | 14·5 | 4·0 |
| 1911 | 100·1 | 79·6 | 3·5 |
| 1911 | 96·5 | 72·4 | 2·5 |

These may be compared with three samples supplied by Professor Greenish which were at least eleven years old, and yielded the following figures :—

| | | | |
|---|---|---|---|
| Crude . . . . | 50·6 | 100·4 | 20·6 |
| Strained . . . | 55·2 | 126·6 | 26·3 |
| Purified from above crude | 60·1 | 130·1 | 25·5 |

The extraction of the storax appears to be for the purpose of preparing a concentrated essence of storax stated to be fifty times as strong as the natural product, also for the preparation of cinnamic alcohol, which possesses an agreeable odour resembling that of hyacinth, and is also useful as a fixative. This substance is coming into more extended use, and though it may be obtained by synthetic methods, still the odour of the naturally produced alcohol is superior for perfumery purposes.

The characters and tests for the purity of storax are given. The acid value should lie between 60 and 90, and the ester value between 110 and 140. Heated on a water bath for one hour it should not lose more than 5 per cent., and on boiling with sulphuric acid and potassium bichromate it should evolve an odour of oil of bitter almonds.

The total free and combined cinnamic acid is determined after saponification by evaporating off the alcohol, dissolving the residue in water, transferring to a separator and washing with 10 c.c. of ether, which is rejected. The cinnamic acid is liberated by acidifying the aqueous solution with normal sulphuric acid, dissolved in ether, evaporated to dryness, and the residue extracted with 100 c.c. of boiling distilled water. After filtration the solution is allowed to cool to 15° C. and the crystals of cinnamic acid collected on a tared filter paper, dried at 100° C. and weighed. The residue on the original filter is twice extracted with boiling water, and any crystals which separate added to the main bulk. A correction of 0·030 grm. is made for solubility. The amount of cinnamic acid yielded by this method should be at least 15 per cent., the best samples yielding 20 to 25 per cent.

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## 38. Tacamahac.

*Resina Tacamahaca.*

**Origin and Habitat.**—American and West Indian tacamahac is derived from *Icica heptaphyllum* and *Elaphyrum tomentosum* (Burseraceæ); East Indian tacamahac, from *Calophyllum inophyllum*; Bourbon tacamahac, from C. *Tacamahaca* (Burseraceæ). Usually the origin is uncertain. East Indies, Mascarenes, America.

**Chemical Constituents.**—The composition is similar to elemi and anime.

Tacamahaca elemi resin from the Philippines has been examined by A. Tschirch and O. Saal. It had acid number 35·5 and saponification number 65·2. Treated by the usual method it yielded a-isotacelemic acid ($C_{37}H_{36}O_4$, M.P. 120°–121°), 5 per cent.; tacelemic acid ($C_{37}H_{36}O_4$, M.P. 215°), 2 per cent.; $\beta$-isotacelemic acid ($C_{37}H_{56}O_4$, M.P. 120°), 3 per cent.; essential oil (B.P. chiefly 170°–175°), 2 per cent.; *a*- and $\beta$ tacamyrin ($C_{30}H_{50}O$, M.P. 170°), 30–35 per cent.; tacelemesene $(C_{15}H_{24}O)n$, M.P. 75°, 30–35 per cent.; bitter substance, 0·5 per cent.; impurities, 15 per cent.

A sample regarded as genuine tacamahac has also been examined by the same authors. This melted at 85°–87°, had acid value 8·8, and saponification value 36·4. It yielded:

tacaelemic acid ($C_{43}H_{72}O_2$, M.P. 95°), 0·5 per cent.; tacamaholic acid ($C_{15}H_{25}O_2$, M.P. 104°–106°), 0·5 per cent.; essential oil (B.P. mostly at 170°–175°), 3 per cent.; $\alpha$-takoresene ($C_{21}H_{33}O$, M.P. 93°–95°), 50 per cent.; $\beta$-takoresene ($C_{15}H_{25}O$, M.P. 82°), 30 per cent.; bitter substance, 0·5 per cent.; gum ($C_6H_{10}O_5$), 3 per cent.; and impurities, 10 per cent.

**General Properties and Commercial Varieties.**—Tacamahac is usually named "West Indian anime"; nevertheless, anime (*q. v.* and under Elemi) is a decidedly distinct, though similar, resin.

East Indian tacamahac (*alba, orientalis*) is a yellowish grey-brown, semi-transparent, soft, and sticky resin, with greasy lustre, an aroma of lavender, and bitter spicy flavour.

Bourbon tacamahac ("Marienbalsam") is a soft, dark bluish green, sticky resin, smelling rather like Fenugreek, and only partly soluble in alcohol. It is considered by some as identical with Caranna resin (*q. v.*), an opinion that has, however, been questioned of late.

American tacamahac (*occidentalis*) is a solid resin, consisting of masses of variable size, somewhat transparent, brown, easily crumbled, with a smooth, lustrous fracture. At the present time, *Tacamahaca alba* is the sole commercial variety. A similar resin, from *Calophyllum Calaba*, is known as "*Resina ocuje*," but is not met with in commerce.

**Adulterants.**—*Resina anime*, various grades of elemis, and other allied and similar resins.

**Analysis.**—Hirschsohn determined the proportion soluble in hot petroleum ether, dried at 120° C., with the following results :—

| | | |
|---|---|---|
| Tacamahaca orientalis . . | 44·11 per cent. | soluble. |
| Blackish grey tacamahac . . | 52·93 ,, | |
| Do. do. . . | 26·99 ,, | |
| Tacamahaca Mexicana . . | 69·64 ,, | |

E. Dieterich determined the iodine value of *Tacamahaca alba* and found it to range from 70·93–77·72, and the author obtained the subjoined values during a recent examination of several kinds :—

| | Acid Value (direct). | Ester Value. | Saponification Value (hot). |
|---|---|---|---|
| Bourbon tacamahac . | 38·10 | 68·22 | 106·32 |
| | 39·06 | 78·47 | 117·53 |
| West Indian do. . | 28·40 | 68·43 | 96·83 |
| | 22·71 | 75·88 | 98·59 |
| Do. do. . | 20·39 | 77·33 | 97·72 |
| | 27·75 | 95·15 | 122·90 |
| East Indian do. . | 32·99 | 38·81 | 71·80 |
| | 34·43 | 36·57 | 71·00 |
| Do. do. . | 21·41 | 32·67 | 54·08 |
| | 21·37 | 37·58 | 58·95 |
| Do. do. . | 22·20 | 60·90 | 83·10 |
| | 22·60 | 66·31 | 88·91 |

As tacamahac resins are very impure, and probably more or less artificial mixtures, the fluctuations exhibited by the several kinds need cause no surprise. It is noteworthy that the East Indian kinds furnish lower values than those from the West Indies.

All the above figures were obtained by the usual method. The values previously obtained by the author with the cold saponification process (20–50) are untenable, tacamahac being to a large extent unsaponifiable in the cold. At the time these were determined there were no other figures available for comparison.

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## 39. Thapsia Resin.

*Resina Thapsiæ*

**Origin and Habitat.**—*Thapsia garganica*, L. (Umbelliferæ). North Africa, Southern Europe.

**Chemical Constituents.**—The plant contains a milky sap, which furnishes a non-nitrogenous, blistering substance, crystallising in small plates, and melting at 87° C.; caprylic acid and dibasic thapsic acid ($C_{16}H_{30}O_4$) are also present. The active, French commercial extract from the root contains thapsic acid, ethereal oil, 66 per cent. of resin, euphorbon, cholesterin, isocholesterin, gum, fat, aliphatic acids, a terpene which boils at 180° C., a camphene boiling at 170° C., and water. The euphorbon may originate in an admixture of euphorbium (Canzoneri).

**General Properties and Commercial Varieties.**—The resin from the plant or root is a dark, opaque, turbid extract, generally containing water. It has a highly disagreeable smell, and is for the most part soluble in alcohol, carbon disulphide, chloroform, and ether, but only partly so in benzine and petroleum ether.

Water and alcohol are generally employed for the extraction, and additions of extract from *Thapsia villosa* and euphorbium are also made. The extract from *T. villosa* also contains acrid substances soluble in petroleum ether, but is milder in its action than that from *T. garganica*.

The pure French commercial grades act more rapidly than those found in the German market.

Leroux (*Bulletin Commer.*, 1899, 27, p. 417) reports on the extraction and dangerous nature of this resin (agreeing with the author's remarks, *q. v.*), and gives the following additional particulars as to its properties :—

" *Thapsia garganica* is a large umbellifer, indigenous to

Algiers, and is chiefly found in the uplands, associated with *T. decussata.* The active blistering principle is mainly found in the root skin of the plant. The alcoholic extract of the central portion of both varieties is insoluble in water, and that from the bark of *T. garganica* is, for the most part, insoluble in this liquid. The green leaves induce redness when applied to the skin, and great care is necessary in extracting the resin from the roots of *T. garganica;* so that the outer skin of the fresh roots has to be taken off under water (see the author's method under Thapsia resin). The resin is generally obtained by distilling the preparation resulting from the treatment of the more or less pulverised rind with 80–90 per cent. alcohol. The preparation is frothy and fluorescent, owing to the presence of saponin, which is difficult of removal. Benzol is a better solvent of the resin than alcohol, and gives a better product. On evaporation, the benzol preparation leaves the resin as a brown, transparent, pasty mass, whereas the alcoholic preparation yields an opaque, pale mass, of the consistence of honey, which, when treated with benzol, is converted into the resin. Thapsia resin is insoluble in ethereal oils or petroleum benzine."

**Adulterants.**—Inferior resins devoid of stimulating properties, euphorbium, and resin from *T. villosa.*

**Analysis.**—Apart from various reports on the admixture of the less effectual resin from *T. villosa* and of euphorbium, there are practically no analytical data available on Thapsia resin.

It was not until recently that the investigation of Thapsia resin was undertaken by the author, and a method elaborated which, on the one hand, enables the operation to be carried on in safety, and, on the other hand, has given material for the first foundations of a system of valuing and judging the product.

As even the mere heating or evaporating of a Thapsia solution, etc., entails great danger to the operator—extremely painful itching inflammation—the author has borne this in mind, and avoided in his method working with hot liquids or evaporating, except under suitable precautions.

The method comprises—

(*a*) Estimating the percentage soluble in petroleum ether.
(*b*) Hot saponification value of this portion, referred to 1 grm.
(*c*) Estimating the percentage soluble in alcohol.
(*d*) Estimating the percentage insoluble in alcohol.
(*e*) Hot saponification value of the portion soluble in alcohol, referred to 1 grm.
(*f*) Total hot saponification value of the original resin.
(*g*) Percentage of water.
(*h*) Ash content.

About 1 grm. of Thapsia resin is mixed with a sufficient amount of pure sand, and the crumbled mass placed in a Schleicher and Schüll cartridge, the weight of cartridge + sand + resin being noted, as well as that of the cartr dge + sand, and of the resin by itself. The whole is then treated, in a Soxhlet extractor, with petroleum ether for three hours, and, after cooling, the cartridge is removed and dried in the oven at 80° C. until no further odour of petroleum ether is discernible; longer drying must be avoided in view of the moisture-content of the resin. The cold petroleum ether extract is next treated with 20 c.c. of alcoholic $\frac{n}{2}$ caustic potash and boiled for half an hour under a reflux condenser, the apparatus being tightly stoppered. After cooling, the *saponification value of the portion soluble in petroleum ether* is determined by the usual method (see Introduction to Part II.), and the results are referred to 1 grm.

*The percentage soluble in petroleum ether* is found, indirectly, by calculation, from the loss in weight of the aforesaid cartridge, and expressed as a percentage. The cartridge is then replaced in the extractor, and, after charging the flask with 20 c.c. of alcoholic $\frac{n}{2}$ caustic potash and 50 c.c. of alcohol, is extracted for two hours longer. The alcohol serves as the extracting reagent, whilst the underlying alkali immediately saponifies the dissolved substances. After two hours the whole apparatus is cooled, and the cartridge is then dried at 100° C. until constant in weight.

The extra loss in weight, calculated in percentages, gives the value of the *portion soluble in alcohol ;* the residue, which is easily calculated by deducting the weight of cartridge + sand from the total weight of cartridge + sand + resin, expresses the value, *insoluble residue.*

The saponification liquid in the flask is titrated with acid, and the potash absorbed—calculated to 1 grm.—gives the *saponification value* (*hot*) *of the portion soluble in alcohol.*

The *total saponification value* (*hot*) of the original resin is found by saponifying 1 grm. of the resin with 25 c.c. of alcoholic $\frac{n}{2}$ potash, under a reflux condenser, and titrating back when cold.

The percentages of moisture and ash are determined by known methods, with the precaution, however, that a properly ventilated drying cupboard is used, the draught pipe of which discharges into the open air (this is easily effected by means of rubber piping and glass tubing). The bulk of the active ingredients is in the portion soluble in petroleum ether, only small quantities being found in that soluble in alcohol.

Several commercial varieties, among which may be noted three pure French resins, and two inferior German commercial specimens, gave the values recorded in the following table :—

| Thapsia Resin. | Water % | Ash % | Soluble in Petroleum Ether % 3 | Sapon. Val., h., of No. 3, cal. to 1 grm. | Soluble in Alcohol % 5 | Sapon. Val., h., of No. 5, cal. to 1 grm. | Residue insoluble in Alcohol % | Total Sapon. Val., h., of Crude Res. |
|---|---|---|---|---|---|---|---|---|
| No. I. Pure, of French origin, very strong— | | | | | | | | |
| Cal. to undried drug . . | 10·336 | 0·403 | 23·02 | 225·90 | 74·83 | 340·17 | 2·15 | 301·57<br>326·99 |
| Do. anhydrous drug . . | — | 0·450 | 25·67 | 251·94 | 83·46 | 379·38 | 2·40 | 336·33<br>364·68 |
| No. II. Pure, French, very strong— | | | | | | | | |
| Cal. to undried drug . . | 7·916 | 0·415 | 17·75 | 332·60 | 82·25 | 338·74 | 0·00 | 317·55<br>333·24 |
| Do. anhydrous drug . . | — | 0·451 | 19·28 | 360·18 | 89·32 | 367·86 | 0·00 | 344·84<br>361·88 |
| No. III. Pure, of French origin— | | | | | | | | |
| Cal. to undried drug . . | 7·43 | 0·16 | 19·73 | 282·83 | 72·81 | 375·42 | 0·199 | 353·68<br>355·89 |
| Do. anhydrous drug . . | — | 0·173 | 21·31 | 305·53 | 86·71 | 405·55 | 0·215 | 383·07<br>384·47 |
| No. IV. Origin doubtful, less strong— | | | | | | | | |
| Cal. to undried drug . . | 32·38 | 0·388 | 42·45<br>44·03 | 114·38<br>113·04 | 56·67<br>53·78 | 383·80<br>384·41 | 0·88<br>2·19 | 255·11<br>265·17 |
| Do. anhydrous drug . . | — | 0·574 | 62·78<br>65·12 | 169·15<br>167·17 | 83·81<br>79·35 | 567·59<br>568·49 | 1·80<br>3·24 | 377·78<br>392·15 |
| No. V. Origin doubtful, obtained from a German firm. Poor— | | | | | | | | |
| Cal. to undried drug . . | 9·032 | 0·380 | 38·22<br>42·02 | 249·21<br>236·59 | —<br>— | 335·54<br>341·72 | — | 290·76 |
| Do. anhydrous drug . . | — | 0·418 | 42·02<br>46·00 | 273·96<br>260·08 | —<br>— | 368·68<br>375·65 | — | 319·63 |

These values furnish the subjoined maximum, minimum, and mean values for the *pure*, active resin, calculated to the anhydrous drug—

| | I. | II. | |
|---|---|---|---|
| | Maximum and Minimum Limits. Per cent. | Mean. Per cent. | Or in Round Numbers. Per cent. |
| Water . . . . | 7·43– 10·336 | 8·88 | 9 |
| Ash . . . . . | 0·16– 0·415 | 0·2875 | 0·3 |
| Soluble in petroleum ether . | 19·28– 25·67 | 22·475 | 22·5 |
| Sapon. val., h., of same, cal. to 1 grm. | 251·94–360·18 | 306·06 | 305 |
| Soluble in alcohol . . . | 83·46– 89·32 | 86·39 | 86·5 |
| Sapon. val., h., of same, cal. to 1 grm. | 367·86–405·55 | 386·05 | 386 |
| Residue insoluble in alcohol . | 0·00– 2·40 | 1·2 | — |
| Total saponification value, h. . | 336·33–384·47 | 360·40 | 360 |

In contrast to these figures No. IV. in the Table shows an abnormally high percentage of water, and a very high percentage soluble in petroleum ether, with a very low saponification value, for same; resin No. V. shows a very high percentage soluble in petroleum ether, with a low saponification value, for the same, as also a very low total saponification value. Although, on the basis of these researches, the author does not venture to assume that there is any direct connection between these abnormal values and the activity of the corresponding resins, he nevertheless considers it advisable to give special prominence to these divergent and fluctuating figures, and contrasts them with the relatively harmonious values of the pure and efficacious specimens of Thapsia resin, which vary within more restricted limits.

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## 40. Turpentine.

*Terebenthina, Balsamum Terebinthinæ* (officinal in Germ. Pharm. III.).

### I. Ordinary Turpentine.

**Origin and Habitat.**—Numerous varieties of *Pinus*, such as *P. pinaster*, *P. Laricio*, etc. (Abietineæ). Europe.

**Chemical Constituents.**—Abieto-pimaric acid, water, oil of turpentine, and bitter principle. Tschirch has recently isolated new "crystalline resinol acids" from the resins from *Pinus palustris*, *Picea vulgaris*, *Abies pectinata*, by fractional solution (see *Ph. Ztg.*, 1899, No. 77), also below.

### II. Larch-Venice Turpentine.

**Origin and Habitat.**—*Larix decidua*, M. (Abietineæ). Europe.

**Chemical Constituents.**—Laricinolic acid ($C_{20}H_{30}O_2$, M.P. 147°–148°), 4–5 per cent.; $\alpha$- and $\beta$-larinolic acids ($C_{18}H_{26}O_2$), 55–60 per cent.; resene, 14–15 per cent.; colouring matter and impurities, 2–4 per cent.; succinic acid, 0·1–0·12 per cent. According to Bamberger and Landseidel, the resin of the larch contains a resinol-lariciresinol ($C_{14}H_{10}(OCH_3)_2(OH)_3$) similar to although not identical with pinoresinol; ethereal oil ($C_{10}H_{16}$, B.P. 170°) 15–20 per cent.—less volatile oil (B.P. 190°), 5–6 per cent.—caffeic acid, vanillin, ferulaic acid (?), water, bitter principle, formic acid (Tschirch and Weigel).

**General Properties and Commercial Varieties.**—The ordinary turpentine is thin (to thick) flowing, crystalline, with a strong smell of oil of turpentine, and setting hard immediately in contact with calcium hydroxide (2

parts to 10 of turpentine). Whereas the ordinary turpentines are of balsamic consistence, the pine resins—*Resina Pini* (*q. v.*), which is also obtained from varieties of *Pinus*—are more solid.

*Venice turpentine* is a yellowish or greenish viscous liquid with a pleasant odour, almost perfectly clear; it does not become crystalline, nor does it set immediately when mixed with calcium hydroxide.

*Strasburg turpentine*, from the silver fir, *Pinus picea* (*Abies pectinata*), is thin, clear, yellow, and slightly fluorescent, and has an odour somewhat like that of lemons. Tschirch and Weigel have obtained from Strasburg turpentine: Abienic acid ($C_{13}H_{20}O_2$, M.P. 114°–115°), 8–10 per cent.; abietolic acid ($C_{20}H_{28}O_2$, M.P. 145°–153°), 1.5–2 per cent.; $\alpha$-abietinolic acid ($C_{16}H_{24}O_2$, M.P. 95°–96°); $\beta$-abietinolic acid (M.P. 93°–94°), 46–50 per cent.; easily volatile essential oil (B.P. 162°–163°), 24–25 per cent.; less volatile oil 4–6 per cent.; abietoresen ($C_{19}H_{13}O$, M.P. 168°–169°), 12–16 per cent.; alkaloid, colouring matter, water 1–2 per cent.; succinic acid ·05–·08 per cent.

*Chios turpentine* is like mastic (*q. v.*), and comes from species of *Pistacia*.

*Russian turpentine*, from *Pinus sylvestris*, contains, according to Schkatelow, 30 per cent. of a dry, crystalline acid ($C_{40}H_{58}O_5$).

*Canada balsam* and *Mecca balsam* (*q. v.*) are also turpentines in the wider sense of the term. (For *Terebinthina cocta*, see *Resina Pini*). A turpentine of sharp, acrid flavour, and containing succinic and abietic acid is fuirnshed, according to Hartwich, by the Mexican *Pinus religiosa* (Abietineæ) and is known as "Aceite de abeto." *Carpathian balsam*, or *Balsamum Carpathicum*, comes from *Pinus Cembra*, L.

**Adulterants and Substitutes.**—Artificial mixtures of resin, oil of turpentine, and water.

**Analysis.**—The chief varieties that have been subjected to analytical examination are Chios turpentine, ordinary turpentine from various sources, Venice turpentine, and Russian turpentine. Artificial commercial products have also been tested, and Strasburg turpentine, Canada balsam, and Mecca balsam (*q. v.*) have been described. The reason why the turpentines are not included with the balsams in the present work, in contradistinction to a usual practice, is that, instead of being solutions of resins in ethereal oils like most of the balsams, the turpentines are very thick and viscid mixtures, which are partly crystalline, and are more nearly allied to the resins than to the balsams, though much softer than the almost perfectly solid pine resins (*q. v.*) met with in commerce. This also applies to storax (*q. v.*).

The analysis of the turpentines will be dealt with in the following order :—

I. Ordinary turpentines.
II. Larch turpentine.
III. Chios turpentine.
IV. Strasburg turpentine.

### I. Ordinary Turpentines

Hirschsohn found that the turpentines dissolve in petroleum ether, except for a slight residue.

Kremel found—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . . . | 128·7 | 124·4 |

He did not estimate any other values.

E. Dieterich found—

(*a*) *Terebinthina communis* (*Abietina*)—

| | |
|---|---|
| Acid value (direct) | 112·45–136·81 |
| Ester value | 9·84– 32·75 |
| Saponification value (hot) | 139·77–160·93 |

(*b*) *Terebinthina communis* (*Gallica*)—

| | |
|---|---|
| Acid value (direct) | 104·72–140·93 |
| Ester value | 2·80– 9·80 |
| Saponification value (hot) | 108·99–149·33 |

Solubility in—

| | |
|---|---|
| Alcohol (90 per cent.) | complete. |
| Ether | ,, |
| Chloroform | ,, |
| Acetic ether | ,, |
| Benzol | ,, |
| Oil of turpentine | ,, |
| Carbon disulphide | almost complete. |
| Petroleum ether | 94·04–95·71% |

(*c*) *Terebinthina communis* (*Pinus Cembræ*)—

| | |
|---|---|
| Acid value (direct) | 117·03–118·56 |
| Ester value | 56·01– 60·19 |
| Saponification value (hot) | 167·40–179·53 |

(*d*) *Terebinthina communis* (*Pinus sylvestris*)—

| | |
|---|---|
| Acid value (direct) | 128·65–144·94 |
| Ester value | 34·59– 38·75 |
| Saponification value (hot) | 167·40–179·53 |

All these values were determined by the usual method, except that the saponification liquid was first evaporated, and then taken up again with alcohol for reverse titration.

K. Dieterich found—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Acid value (direct) | 107·98 | 107·69 | 112·42 | 113·36 |
| Ester value | 10·02 | 7·82 | 17·25 | 20·39 |
| Saponification value (hot) | 118·00 | 115·51 | 129·67 | 133·65 |

and later—

| | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| Acid value (direct) | 112·93 | 115·13 | 115·32 | 114·84 | 115·88 |
| Ester value | 7·77 | 6·30 | 7·15 | 4·29 | 4·14 |
| Sapon. value (hot) | 120·70 | 121·43 | 122·47 | 119·13 | 120·02 |

Dietze found for French turpentine—

| | |
|---|---|
| Acid value (direct) | 119·67–120·41 |
| Ester value | 1·76– 3·05 |
| Saponification value (hot) | 121·43–123·46 |

These values agree well with those found by E. Dieterich (see above, *T. communis Gallica*).

Kitt determined the carbonyl value of resin from *Pinus halepense*, and found—

| | I. | II. |
|---|---|---|
| Carbonyl value | 0·28 | 0·57 |

The author determined the acetyl values for ordinary turpentine, with the following results :—

| | | |
|---|---|---|
| Acetyl | Acid value | 123·75–125·55 |
| | Ester value | 62·32– 93·79 |
| | Saponification value | 187·87–217·04 |

the acetylised product being solid, though the original substance is viscid.

(For the value of the carbonyl and acetyl values, see *Chem. Rev.*, 1898, No. 10.)

The chief distinction between ordinary and Venice

turpentine is in the higher acid value of the former. Schkatelow has reported on the chemical data of the above-mentioned Russian turpentine from *Pinus sylvestris* (see the values given by E. Dieterich, under *d*), but not on the analytical details. As a rule, all the pine (*Pinus*) turpentines give the same values, and are distinguishable solely by their outward appearance, their solubility in ether and alcohol being almost identical.

In contrast to colophony, which forms the distillation residue from turpentine, all the turpentines and pine resins (*q. v.*) contain ester compounds, which pass over, either as such or in the form of decomposition products, on distillation, leaving colophony (*q. v.*) behind as an ester-free but etheriferous and lactoniferous resin, with or without traces of ethereal oil.

(For the German Pharmacopœia (III.) tests for turpentine, see *Ph. C.*, 1898, No. 20.)

## II. Larch Turpentine

Being a more valuable product, Venice turpentine has been more closely investigated than ordinary turpentine, and the analytical values obtained harmonise very well and are fairly exact. It has a sp. gr. of 1·060 to 1·190 at 15° and yields on the average 15 per cent. of volatile oil ($C_{10}H_{16}$) consisting almost entirely of pinene.

Hirschsohn found that larch turpentine is almost completely soluble in petroleum spirit. It consists of about 70 per cent. of resin, 15 per cent. of volatile oil and 15 per cent. of resene.

A. Kremel found—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . . . | 68·4 | 70·3 |

Von Schmidt and Erban's results are as follows:—

| | | |
|---|---|---|
| Acid value (direct) | 70·1 | 67·7 |
| Ester value | 32·5 | 29·8 |
| Saponification value (hot) | 102·6 | 97·5 |
| Iodine value | 145·3 | — |

Solubility in—

Alcohol, Ether, Methyl alcohol, Amyl alcohol, Benzol } complete.
Petroleum ether—almost complete.
Acetone, Glacial acetic acid, Chloroform } complete.
Carbon disulphide—partial.
Oil of turpentine—complete.

Beckurts and Brüche examined a number of samples with the following results:—

| | I. | II. | III. | IV. | V. | VI. | VII. |
|---|---|---|---|---|---|---|---|
| Sp. gr. | 1·091 | 1·121 | 1·160 | 1·100 | 1·180 | 1·190 | 1·060 |
| Acid val. (direct) | 85 | 76 | 81 | 94 | 101 | 98 | 93 |
| Ester value | 9 | 5 | 0 | 3 | 0 | 0 | 6 |
| Sapon. val. (hot) | 85 | 81 | 81 | 97 | 101 | 98 | 99 |

Iodine value . . . . . 137–149

Mills and Muter found for genuine Venice turpentine acid value 73·9, saponification value 121·8, and iodine value 109·6; and for a spurious sample acid value 103·0, saponification value 117·6, iodine value 109·6.

E. Dieterich's results are given below—

| | |
|---|---|
| Acid value (direct) | 64·44– 76·69 |
| Ester value | 35·41– 55·94 |
| Saponification value (hot) | 108·27–132·63 |

Solubility in—

Alcohol (90%), Chloroform, Acetic ether, Benzol, Oil of turpentine } complete.
Carbon disulphide—almost complete.
Petroleum ether—98·89 to 100 per cent.
Ether—almost complete.

In determining the saponification value the liquid was evaporated, taken up again with alcohol, and then titrated. The acid value was found by direct titration of the alcoholic solution. The solubilities agree with those of von Schmidt and Erban (see above).

The author obtained the following figures:—

| | |
|---|---|
| Acid value (direct) | 66·93– 68·85 |
| Ester value | 46·27– 54·94 |
| Saponification value (hot) | 114·56–127·71 |

The figures agree well with those found by other authors.

The acetyl values of Venice turpentine were also determined and found to be—

| | | |
|---|---|---|
| Acetyl | Acid value | 69·87– 72·19 |
| | Ester value | 109·08–118·67 |
| | Saponification value | 178·95–190·86 |

Evans' found—

| | |
|---|---|
| Acid value | 70–105·1 |
| Saponification value | 112–123·5 |
| Ester value | 18·4– 49 |
| Refractive index at 15° | 1·5186–1·5195 |

Both Gregor and Bamberger obtained negative results with the methoxyl value test.

The chief adulterants of larch turpentine are artificial preparations, ordinary pine turpentines, and extraneous resins.

Hoffmann has reported on artificial Venice turpentine which he declares to be a product free from oil of turpentine, and of altogether different behaviour. According to Schaal, an artificial turpentine of this class is prepared, from conifer resins, by distillation *in vacuo* at 270° C., and subsequent distillation with oil of turpentine under reduced pressure.

E. Dieterich examined an artificial product of this kind, and found—acid value (direct), 98·79; ester value, 0·88; saponification value (hot), 97·66.

Von Itallie remarks as follows :—

" In the *H. A.*, 1893, E. Dieterich mentions solutions of rosin in rosin oil, which are sold as *Terebinthina veneta*, and that their acid and saponification values are almost identical, whereas in genuine turpentine the acid value is about 70, and the saponification value, 120.

" I received two kinds of turpentine which gave the following values :—

| Acid Value (direct). | Saponification Value (hot). |
|---|---|
| 97·0 | 108·0 |
| 99·5 | 109·3 |

these were therefore mixtures, consisting mainly of rosin and rosin oil."

With regard to the detection of ordinary turpentine in larch turpentine, Hirschsohn says :—

" To detect ordinary turpentine in larch (Venice) turpentine, the Hübl saponification method, recommended by some, is unsuitable, because the acid and ester values thereby obtained vary very considerably, both in the case of ordinary turpentine, and of larch turpentine as well."

On the other hand, Hirschsohn discovered, in the behaviour of turpentine towards ammonia, a means said to be not only capable of distinguishing between ordinary and larch turpentine, but also, to some extent, of detecting the presence of the former in the latter.

"When a small quantity of ordinary turpentine is mixed in a test glass with strong ammonia (sp. gr. 0·96), it gradually distributes itself throughout the liquid to form a milky emulsion; whereas, if larch turpentine be treated in the same manner, the liquid remains clear. On attempting to distribute the turpentine through the liquid by means of a glass rod, it is found that larch turpentine apparently remains unchanged at first, as an oily mass in the aqueous liquid, but afterwards it is converted into a semi-solid, colourless, opaque mass, the liquid being only slightly turbid; ordinary turpentine, on the other hand, immediately distributes in the form of an emulsion, which soon sets to a jelly, especially when the proportion of turpentine to ammonia is about 1 : 5. Larch turpentine, containing 50 per cent. of ordinary turpentine, readily distributes in ammonia, the mixture solidifying in about five minutes, and clarifying when placed in hot water; a mixture containing 30 per cent. of ordinary turpentine also distributes easily, solidifies in about ten minutes, and clarifies in the water bath; with 20 per cent. of ordinary turpentine the sample runs to milk very easily, and does not solidify, but clarifies, on the water bath; when the proportion of ordinary turpentine is less than 20 per cent. it cannot be detected, unless an undoubtedly pure larch turpentine be at hand for comparison.

"Mixtures of larch turpentine with not less than 30 per cent. of ordinary turpentine can be recognised with a fair degree of certainty by means of 80 per cent. alcohol. If

1 part of turpentine be mixed with 3 parts of alcohol and then shaken, larch turpentine gives an almost clear solution, whereas more than half of the total quantity of ordinary turpentine present separates out in a short time."

Although this method of Hirschsohn is not free from objection, and its indications are in nowise to be considered superior to those of the acid, ester, and saponification values, it may nevertheless find a place here as a confirmatory test in doubtful cases. The importance of the acid, ester, and saponification values is evident from the circumstance that ordinary turpentine has a much higher acid value than Venice turpentine; so that large additions of ordinary turpentine to the latter may be recognised by these values. The acetyl acid value of ordinary turpentine is also much higher than that of Venice turpentine, which is an interesting fact, and one indicating the worth of the acetyl values. The quantity of the hydroxyl groups, expressed by the acetyl values, therefore fluctuates according to the amount of the rosin acids present containing hydroxyl. The same remarks also apply to the acetyl-ester and acetyl-saponification values. (With regard to the value of the methoxyl and acetyl values of the resins, see *Chem. Rev.*, 1898, No. 10; and for the Germ. Pharm. tests for turpentine, see *Ph. C.*, 1890, No. 20.)

### III. Chios Turpentine

Though Chios turpentine is often erroneously classed with the *Larix* turpentines, it will be treated separately here, because several reports on it are found in the literature of the subject.

According to Wigner, the following requirements should be fulfilled by Chios turpentine :—

"The sp. gr. is 1·050, but varies, like the consistence, with the percentage of volatile oil. The taste is faintly aromatic, like turpentine, and entirely devoid of bitterness or sharpness; the odour agreeably aromatic, slightly recalling that of turpentine. It is completely soluble in alcohol and ether, only earthy admixtures being left behind. The solution in rectified alcohol is not quite clear, but very little deposit separates on cooling. An admixture of conifer resins can be detected by the solubility test; and an indication is also afforded when the microscopic examination of the residue reveals the pitted vessels so characteristic of coniferous woods. The optical behaviour of Chios turpentine also serves to distinguish it from other kinds of turpentine, the ethereal oil of the former being strongly dextrorotatory, whereas the oils of most conifers give a lævorotation. Conversely, the resins of most conifers are dextrorotatory, that of Chios turpentine being probably lævo-rotatory."

W. Bettink would require Chios turpentine to be completely soluble in boiling alcohol, the solution becoming turbid on cooling. The taste should be neither sharp nor bitter, and the turpentine itself should be devoid of crystals. The mechanical impurities should not exhibit any pitted (conifer) vessels. As this author was in possession of authentic samples, these indications are valuable; above all, the microscopic examination of this turpentine is advisable.

Landerer drew attention long ago to the adulteration of Chios turpentine, finding as much as 20–30 per cent. of sand and stones in the natural product.

Kremel gives the following values for Chios turpentine:—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . . | 47·8 | 53·4 |

but did not determine the saponification value.

E. Dieterich also carefully examined Chios turpentine, and made valuable reports. That he should, however, have treated Chios turpentine as *Terebinthina Laricina*, whereas it is derived from *Pistaceæ*, was a mistake. This Pistacia turpentine is distinguishable from the Pinus and Larix turpentines by the absence of the characteristic pitted vessels, and should on no account be classed with the Larix turpentines.

E. Dieterich found—

| | |
|---|---|
| Acid value (direct) . . . . | 47·13–48·53 |
| Ester value . . . . . | 19·13–21·47 |
| Saponification value (hot) . . . | 66·26–70·00 |

Solubility in—

| | |
|---|---|
| Ether, Chloroform, Acetic ether, Benzol, Oil of turpentine | almost to completely soluble. |
| Alcohol (90 per cent.) . | 98·64 to completely soluble. |
| Carbon disulphide . | almost completely soluble. |
| Petroleum ether . . | 98·49 per cent. to completely soluble. |

## IV. Strasburg Turpentine

(*Terebinthina argentoratensis*)

Though actual analytical data for Strasburg turpentine are lacking, and the article itself has now almost entirely disappeared from the market, it is nevertheless included here for the sake of completeness.

According to Flückiger, the resin sap of the white pine agrees perfectly with Canadian turpentine (see Canada balsam), except as regards solubility, the former being

miscible in all proportions with glacial acetic acid, absolute alcohol, and acetone, to form a clear liquid. The white pine turpentine has also a finer odour, so that it was formerly known in France as *Térébinthine au citron*. The taste has not the sharpness of Canada balsam, and is less bitter. No fluorescence is discernible.

**White Turpentine.**—The white turpentine yields about 17 per cent. of a dextrorotatory volatile oil, sp. gr. 0·864, and Tschirch and Koritschoner separated from it the following constituents: palabienic acid ($C_{13}H_{20}O_2$), 5 per cent.; palabietinic acid ($C_{20}H_{30}O_2$), 6–7 per cent.; $\alpha$- and $\beta$-palabietinloic acids, 53–57 per cent.; essential oil, 20–22 per cent.; paloresene, 10 per cent., with traces of a bitter substance. Both the resin and palabietinic acids are lævorotatory.

**Canada Turpentine.**—Bonastra found in this resin volatile oil 18·6 per cent.; resin easily soluble in alcohol, 46 per cent.; resin not easily dissolved, 33·4 per cent.; caoutchouc similar to sub-resin, 4·0 per cent.; bitter extractives, salts and a trace of acetic acid, 4·9 per cent. A sample examined by Flückiger contained: essential oil ($C_{10}H_{16}$ with a small proportion of an oxygenated oil), 24 per cent.; resin soluble in boiling alcohol, 60 per cent.; resin soluble only in ether, 16 per cent. Tschirch, Weigel, and Bruening isolated from it: Canadinic acid ($C_{19}H_{34}O_2$, M.P. 135°–136°), 16 per cent.; canadolic acid ($C_{19}H_{28}O_2$, M.P. 143°–145°), 0·3 per cent.; and $\alpha$- and $\beta$-canadinolic acids ($C_{19}H_{30}O_2$, M.P. 89°–95°), together 48–50 per cent., the last two predominating considerably; volatile oil (B.P. 160°–167°), 23–24 per cent., and indifferent resene ($C_{21}H_{40}O$, M.P. 170°), 11–12 per cent.

**Bordeaux Turpentine.**—From Bordeaux turpentine Tschirch and Bruening separated: pimarinic acid ($C_{14}H_{22}O_2$),

6–7 per cent.; pimaric acid ($C_{20}H_{30}O_2$), 8–10 per cent.; $\alpha$- and $\beta$-pimarolic acids ($C_{18}H_{26}O_2$), 48–50 per cent.; bordoresen, 5–6 per cent., and traces of succinic acid.

**Finnish Turpentine.**—In Finnish turpentine Tschirch and Niederstadt found: silveolic acid ($C_{14}H_{20}O_2$), 1·5 per cent.; $\alpha$-silvinolic acid ($C_{15}H_{26}O_2$), and $\beta$-silvinolic acid ($C_{14}H_{24}O_2$), together 58–60 per cent.; resene, 20–21 per cent.; volatile oil, 15 per cent. (sp. gr. at 15° 0·840); also traces of a bitter substance and succinic acid.

**Jura Turpentine** from *Picea vulgaris* contains, according to Tschirch and E. Bruening: picea-pimarinic acid ($C_{18}H_{20}O_2$), 2–3 per cent.; piceapimaric acid ($C_{20}H_{30}O_2$), 1·5–2·0 per cent.; $\alpha$- and $\beta$-piceapimarolic acids, 48–50 per cent.; volatile oil, 32–33 per cent.; resene ($C_{21}H_{36}O$), 10–12 per cent., together with traces of colouring matter, bitter substance and succinic acid.

The oleo-resin of *Pinus insularis*, from the Philippine Islands, has been examined by B. T. Brooks, who found that on distillation it yielded a terpene very like ordinary turpentine, 96 per cent. of it distilling between 154° and 165·5°. It had a specific gravity at 30° of 0·8593, refractive index at 20° 1·4656, specific rotation $[a]_D + 26·5°$, and consisted for the most part of pinene.

The resin resembled ordinary colophony, consisting almost entirely of abietic acid. It had a melting point of 154°–156°, saponification number 170·2 and gave the Liebermann-Storch reaction for colophony.

**Oleo-Resin of Abies Cephalonica.**—A sample of this resin examined by E. J. Emmanuel gave the following results: acid number (direct) 113·54, (indirect) 128·31; saponification number (cold) 137·06, (hot) 157·54. It was found to be entirely soluble in alcohol, ether, and chloroform, and on examination by the method of Tschirch it

yielded elatic acid ($C_8H_{12}O_2$, M.P. 124°–126°), elatinic acid ($C_{12}H_{18}O_2$, M.P. 78°–80°), and elatolic acid ($C_9H_{16}O_2$, M.P. 118°–120°), all of which were amorphous, and the last two acids constituted together about 70 per cent. of the oleo-resin. In addition there was present an essential oil, 17·4 per cent., with specific gravity at 15° = 0·9279, refractive index at 13·5° 1·4745, and rotation $[a]_D$ — 68° in 200 mm. tube. By fractional distillation the oil was separated into three portions, boiling respectively between 89°–150°, 150°–155°, and 155°–175°, the first two of which had odour like terpenes, also an amorphous resene (M.P. 92°–96°), and some bitter substance. It is stated that the acids and also the resene responded to the phytosterol reactions.

A. Tschirch and H. Schulz have also examined the oleo-resin of Aleppo pine (*Pinus halepensis*), which they found to be a viscous, semi-fluid material contaminated with extraneous matters, and some pale yellow masses with a crystalline structure which gave the following figures on analysis :—

| | |
|---|---|
| Acid value (direct) . . . . . | 125·9 |
| ,, ,, (indirect) . . . . | 131·75 |
| Saponification value (cold) . . . . | 145·31 |
| ,, ,, (hot) . . . . | 154·15 |

The oleo-resin yielded on further examination : halepopininic acid ($C_{21}H_{32}O_3$), 5 per cent.; halepopinolic acid ($C_{17}H_{26}O_2$) and halepopinitolic acid ($C_{16}H_{26}O_2$), 59 per cent.; essential oil, 21–26 per cent.; resene, 0·6 per cent.; and traces of a bitter substance.

Three samples of turpentine of the Aleppo pine from the South of France and Algeria have been examined by Vèzes, who obtained the following results :—

| | Per cent. |
|---|---|
| Essential oil | 14·7–27·0 |
| Non-volatile (resin) | 66·7–78·3 |
| Solid impurities | 0·8– 6·6 |
| Water and loss | 2·1– 5·5 |

The essential oil had the following characters :—

| | |
|---|---|
| Density at 25° C. | 0·8552–0·8568 |
| Optical rotation $[a]$ = | + 46·6°– + 47·6° |
| Refractive index | 1·4638–1·4652 |

At least 80 per cent. distilled over between 155° and 156°.

The oleo-resin of *Pinus halepensis* from Montpellier has also been examined by Reutter, who found the melting point to be 83°–85° C.; acid value, 180·75–182·74; ester value, 15·7–16·5; saponification value, 196·5–199·3. It dissolved very readily in petroleum ether, oil of turpentine, alcohol, chloroform, and acetone, but was only slightly soluble in carbon bi-sulphide. Ether and benzol dissolved about 75 per cent. It was separated by the method of Tschirch into the following constituents: halepinic acid ($C_{20}H_{40}O_4$, M.P. 73·5°–74·5°), 19 per cent.; halepinolic acid ($C_{40}H_{56}O_5$, M.P. 144·2°–145·5°); $\alpha$-halepinolic acid ($C_{34}H_{50}O_4$, M.P. 80·5°–81·5°); $\beta$-halepinolic acid ($C_{18}H_{28}O_4$, M.P. 80·5°–82°) and haleponic acid ($C_{18}H_{28}O_2$ or $C_{37}H_{58}O_4$, M.P. 156°–157°), together 53 per cent.; soluble in caustic potash; essential oil, 14·4 per cent.; resene, 6·6 per cent.; and vegetable debris, etc., 7 per cent.

**Oleo-Resin of Sand Pine.**—The oleo-resin of the sand pine (*Pinus clausa*), which is a native of Florida, has been examined by A. W. Schorger. It yielded:—

| | Per cent. |
|---|---|
| Volatile oil | 18·93 |
| Resin (Grade G) | 72·30 |
| Trash | 2·67 |
| Water | 6·10 |

Two samples of the volatile oil exhibited the following characters :—

| | I. | II. |
|---|---|---|
| Specific gravity at 15° . . | 0·8725 | 0·8723 |
| Refractive index at 15° . . | 1·4768 | 1·4767 |
| Specific rotation at 20° . . | — 22·49 | — 22·80 |

By careful fractional distillation 60 per cent. of the oil passed over between 162° and 165° and a further 35 per cent. between 165° and 167°. The oil contains 75 per cent. of $\beta$-pinene and 10·1 per cent. of camphene.

**Oleo-Resin from the Norway Pine** (*Pinus resinosa*). —The oleo-resin of the Norway pine has been investigated by G. B. Frankfurter. It had a specific gravity at $\frac{20°}{4°}$ ·8137, refractive index at 20° 1·4788, and a specific rotation at 20° of — 4°. By distillation *in vacuo* it yielded 20 per cent. of an essential oil, the residual resin being a brittle solid, M.P. 81·5°. By dissolving in ether and pouring into 80 per cent. alcohol a crystalline product, melting at 83·7° separated. This was fractionally divided into two products, a resin acid melting at 97°–98° and having the composition $C_{25}H_{36}O_5$. This differed from abietic acid ($C_{19}H_{28}O_2$) both in composition and properties. The second product appeared to be ordinary abietic acid, though the recrystallised acid had a lower melting point (129°–130°) than that usually given. The first named acid differs from the acids so far described, but in some of its properties resembled Tschirch's palabienic acid.

The oleo-resin of *Pinus pinea*, according to Reutter, has the melting point 85° C., acid value 101·7–102·5; ester value 167·54–167·6; and saponification value 269·27–270·1. It dissolves in the following proportions in the solvents named: carbon bisulphide, about 80 per cent.; chloroform and alcohol, 75 per cent.; ether, 66 per cent.; turpentine and benzol, about 25 per cent.; and but slightly in petroleum

ether. By the method of Tschirch it yielded pineic acid ($C_7H_{14}O_4$, M.P. 99°–99·5°), 18 per cent.; pineolic acid ($C_{18}H_{28}O_3$, M.P. 86°), 37 per cent.; essential oil depositing crystals with odour of borneol and M.P. 204°, 12 per cent.; resene ($C_9H_{13}O_4$, M.P. 85°), 18 per cent.; and vegetable debris insoluble in ether, 15 per cent.

**Oleo-Resin of Pinus cambodgiana.**—According to A. Wichmann, the oleo-resin of *Pinus cambodgiana* is a yellowish or greyish-white semi-fluid mass of about the consistency of honey. It has an acid number (direct) of 145·31, and (indirect) 148·12. By steam distillation it yielded 19·35 per cent. of a yellow aromatic volatile oil having a sp. gr. of 0·892, refractive index at 21° 1·48455. From it were obtained by the well-known method of separation, cambopinic acid ($C_{11}H_{18}O_2$, amorphous, M.P. 78°), cambopinonic acid ($C_{16}H_{24}O_2$, amorphous, M.P. 71°), and a small amount of camboresen.

**Gum Resin of Araucaria Cunnighamii.**—R. T. Baker and H. G. Smith have examined a gum resin which exudes from *Araucaria Cunnighamii* of Australia. The best source of the exudation was found to be the stumps of trees which had been felled for some little time; it was then seen to have oozed from between the inner and outer barks. The gum resin was found on analysis to have the following composition :—

| | Per cent. |
|---|---|
| Volatile oil | 3·80 |
| Free acid (calculated as acetic) | 0·13 |
| Gum | 8·00 |
| Resin | 47·00 |
| Nitrogenous substances, etc. | 0·51 |
| Woody fibre | 0·60 |
| Water and undetermined | 39·96 |
| | 100·00 |

The volatile oil obtained by distilling the oleo-resin with steam had: specific gravity at 22° = 0·80577; refractive index at 22° = 1·457; and specific rotation $[a]_D = + 3·2°$. The gum was a galacto-araban and the resin had a specific gravity at 16° of 1·061, acid number 107, and was dextro-rotatory. It contained two acids, the one, having a melting point of 234°–235°, was named dundathic acid, owing to the fact that it was first separated from the "Dundathu pine." This had the formula $C_{21}H_{32}O_3$ and specific rotation $[a]_D = + 55°$. The second acid had a melting point of 84°–85°, and analysis indicated the formula $C_{20}H_{30}O_2$. It is lævorotatory and probably isomeric with abietic acid. The resin also contained a neutral constituent with a specific rotation $[a]_D = - 60·3°$, and a bitter principle which was also lævorotatory and crystallised in microscopic needles. The composition of the resin was approximately: Dundathic acid, 14½ per cent.; isomeric abietic acid, 62 per cent.; neutral resin, bitter principle, etc., 13½ per cent.

**Oleo-Resin of Agathis Robusta.**—R. T. Baker and H. G. Smith have also examined the oleo-resin of *Agathis robusta*, an Australian tree. When freshly exuded this forms a thin semi-fluid mass having the following composition:—

| | Per cent. |
|---|---|
| Essential oil | 11·64 |
| Volatile acids (calculated as acetic) | ·1055 |
| Gum | 2·37 |
| Reducing sugars | 0·62 |
| Resin | 62·00 |
| Nitrogenous matters | 0·20 |
| Water and undetermined | 23·0645 |
| | 100·0000 |

The essential oil had the specific gravity 0·8629 at 16°, refractive index 1·4766 at 16°, and a rotation in 100 mm. tube + 20·2°. It consisted practically of pure pinene. The gum contained manganese and was composed in part of araban. The resin in solution in acetone showed for a 10 per cent. solution in 100 mm. tube the rotation + 3·4°, had a specific gravity at 17° of 1·053, and the acid number 148. It consisted of dundathic acid, 16 per cent.; dundatholic acid ($C_{19}H_{28}O_3$), M.P. 77°, increasing on keeping to 101°–102°; and specific rotation + 21·5°, about 73·2 per cent.; neutral resin, specific rotation + 35·6°, bitter principle, etc., 10·8 per cent.

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## 41. Turpethum Resin.

*Resina Turpethi*

**Origin and Habitat.**—*Ipomœa Turpethum*, R. Brown (Convolvulaceæ). East Indies.

**Chemical Constituents.**—The resin "Turpethin" has been regarded as identical in composition with Scammonin, but, according to Spirgatis, more correctly speaking it is

identical with the Orizabin or Jalapin $C_{34}H_{56}O_{16}$, in Jalapa. This authority also gives Scammonin as identical with Orizabin or Jalapin, and states that Turpethin is a glucoside of the formula $C_{34}H_{56}O_{16}$.

**General Properties and Commercial Varieties.**—A brownish yellow, almost inodorous resin, of sharp and bitter flavour; readily soluble in alcohol, but insoluble in ether. The only variety in the market is the resin extracted from the roots, and sold in sticks.

**Adulterants.**—Vegetable and mineral impurities, and artificial products.

**Analysis.**—Turpethum resin is prepared in the same manner as Jalapa resin and scammonium, by boiling the roots in water, and recovering the resin by means of alcohol.

It is dealt with in this place mainly because, according to Spirgatis, its constituents are identical with Scammonin and Jalapin. It is sold in sticks, has the melting point 183° C., and is distinguishable from scammonium and Jalapa resin by its insolubility in ether, wherein the other two are, for the most part, soluble. All three are soluble in alcohol. As with scammonium and Jalapa resin, the ash content should be minimal.

The author has examined the commercial product (*Resina Turpethi* in sticks) by the usual method, and obtained the following values :—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Acid value (direct) . . | 20·73 | 24·45 | 22·93 | 20·55 |
| Ester value . . . . | 139·98 | 137·27 | 141·01 | 139·94 |
| Saponification value (hot) . | 160·71 | 161·72 | 163·94 | 160·49 |

The various samples, therefore, appear to be fairly uniform in composition.

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## CHAPTER III

### GUM RESINS

As in the case of many of the resins, so with the gum resins, the analytical data hitherto accumulated were, almost without exception, obtained with extracts, and consequently were—as already several times remarked—of only relative worth, since the values furnished by extracts can never correspond to those of the crude product, and are therefore incapable of affording any reliable evidence on the nature of the latter (see Part I.). Nevertheless, these values obtained from extracts will be recorded for the sake of completeness, since they may, in doubtful cases, serve a useful purpose by at least affording an indication of the characteristics of the gum resin extracts. Moreover, values have already been determined for the unaltered crude product in the case of many of the gum resins. It is worthy of special mention that the values furnished by this class of substances exhibit the greatest fluctuations shown by any members of the resin product group, a circumstance in part due to the methods employed, and the use of extracts, but mainly to the very changeable constitution of the gum resins themselves, these being the most variable of all the resinous substances so far as concerns the percentage and mutual relation of their contained ethereal oil, gum, resin, etc. Furthermore, the gum resins show the largest percentage (up to 50 per cent.) of ash and impurities, a circumstance which, in conjunction with their greasy character,

renders the preparation of an average sample for analysis peculiarly difficult. To triturate the gum resins it is first advisable to cool them, either in a cold cellar, or, better, in an ice-chest or refrigerating mixture, the application of warmth, as recommended by the German Pharmacopœia, being not only unsuccessful and impractical, but also irrational, since it causes a loss of ethereal oil. It is necessary to take four or five samples of each gum resin to be analysed, and to calculate the definite values from the results of four or five analyses. The above remarks as to the use of warmth also apply to the so-called "purified gum resins" (by the wet or dry process) which were formerly plentiful in commerce, though now rare. These extracts, though doubtless practical and also relatively pure, are incapable of corresponding to the crude product, except to a very minor degree. It is therefore worthy of recognition that the German Pharmacopœia has, so far, not acknowledged these products, as the Swiss Pharmacopœia has done with the dry gum resins purified by sifting.

## 42. Ammoniacum.

*Gummi-resina ammoniacum* (officinal in Germ. Pharm. III.).

**Origin and Habitat.**—*Dorema ammoniacum* (Umbelliferæ). Persia. *Ferula communis.* Morocco, Cyrenaica.

**Chemical Constituents.**—Matters insoluble in water or alcohol, 3·5 per cent.; acid and neutral resin (total, 69 per cent.); soluble gum, 22·7; insoluble, 3·5; water, 4·4. Both kinds of resin are free from sulphur. The acid resin is a salicylic ammoresinotannol ester (Luz); and the isolated ammoresinotannol has the formula $C_6H_{10}O$, or $C_{18}H_{29}O_2OH$, so that it is analogous in composition with galboresinotannol

(see Galbanum). Ethereal oil (0·2–0·4 per cent.) is also present, and salicylic acid in traces; but no umbelliferon or sulphur. Volatile acids such as valeric and butyric are also found (Tschirch and Luz). The gum ($2C_6H_{10}O_5C_5H_8O_4$, 12–16 per cent.) is similar to gum arabic, is free from nitrogen, and yields on hydrolysis galactose, arabinose (16·60 per cent.), and probably mannose (Frischmuth). Resin 47·2 to 72·0 per cent., and gum 18·4 to 26·1 per cent.

**General Properties and Commercial Varieties.**—*Persian ammoniacum* is in the form of greyish white masses or tears, yellow externally and white within, with a waxy lustre. In the cold it is brittle and of peculiar aromatic odour. The variety *in massa* contains more ethereal oil than the *in lacrymis* grade; the former being therefore greasy, whilst the latter is solid. Ammoniacum "in tears" is also the purer kind, but, owing to its lower percentage of ethereal oil, is not to be regarded as superior to the other, especially for pharmaceutical purposes. Persian ammoniacum—which is the most usual commercial quality—is but partially soluble in water or alcohol.

*African ammoniacum*, from *Ferula tingitana*, bears only a very slight external resemblance to the Persian drug; it is much darker in colour, more impure, and has quite a different taste and smell. Only one grade, *in massa*, appears to exist. It also differs from Persian ammoniacum in giving the umbelliferon reaction with hydrochloric acid and ammonia (see Galbanum), and again by its analytical constants, in which respect it also differs from galbanum.

**Adulterants, etc.**—Galbanum, African ammoniacum, inferior resins, vegetable detritus, etc., from which it is sometimes separated by melting and straining, forming ammoniacum colatum.

**Analysis.**—Frequent reference has been made by

various authors to the impurity of ammoniacum, particularly with regard to the mineral matter. E. Dieterich on this account recommended the use of the selected or purified drug, and urged its adoption for the Pharmacopœia. Even though it be possible to reduce the percentage of ash and impurities by purification, the objections mentioned in the Introduction to this Section—and especially those relating to "purified gum resins"—still hold good. The Danish Pharmacopœia rightly prescribes that ammoniacum should be powdered in the cooled state (see also Introductory Remarks). Neither the adoption of a purified grade, as advocated by E. Dieterich and Thoms, for the Pharmacopœia, nor the heating of the product is helpful in this direction, the sole remedy being the strict regulation of the ash content and the percentage soluble and insoluble in alcohol, as frequently urged by the author. The best reactions for this drug are those of Picards and Plugge, and, in addition, the author's test as applied to galbanum. Picards found that the alcoholic solution of this gum resin gives a beautiful violet coloration with sodium hypochlorite. Plugge recommends sodium hypobromite, and claims to have detected as low as 1 per cent. of ammoniacum in galbanum and other mixtures. The author, however, has not been able to confirm this; but the samples tested were highly impure kinds, which gave merely dirty, and by no means characteristic, colour reactions. Consequently, like other colour reactions, this test can only be considered as of relative value. As previously stated under Galbanum, the detection of ammoniacum in this drug is possible by the quantitative method. Plugge also endeavoured to determine quantitatively the amount of ammoniacum in mixtures by means of a standardised solution of bromine. His researches revealed the following constituents in am-

moniacum, the figures found previously by other authorities being added to the Table, for purposes of comparison :—

| Constituents. | Plugge. | Buchholz. | Braconnot. | Moss. | Hirschsohn. |
|---|---|---|---|---|---|
| | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. |
| Ethereal oil . . | 1·27 | 4·0 | 7·2 | 2·8 | 1·43– 6·68 |
| Moisture . . . | 5·10 | | | | 0·81– 3·27 |
| Ash . . . . | 2·00 | | | 2·3 | 2·02–16·88 |
| Resin . . . | 65·53 | 72·0 | 70·0 | 68·6 | 47·12–69·22 |
| Gum . . . | 26·10 | 22·4 | 18·4 | 19·3 | — |
| Bassorin . . . | — | 1·6 | — | — | — |
| Gelatinous substances. | | — | 4·4 | 5·4 | — |
| Extractives . . | — | — | — | 1·6 | — |
| Sugar, etc. . . | — | — | — | — | 1·61– 4·59 |
| Per cent. sol. in water | — | — | — | — | 11·85–25·74 |
| Residue . . . | — | — | — | — | 0·81– 3·09 |

Hirschsohn laid down as requirements to be exacted of the Persian grades that the *in massa* mark should contain at least 55 per cent. of material soluble in petroleum ether, and the *in granis* kind not less than 66 per cent., the ash content being fixed at 3 per cent. (This is a limit which probably only very few *in massa* specimens nowadays exhibit.) The comprehensive researches on ammoniacum have been supplemented by numerous qualitative reactions, one of which enables Persian galbanum to be distinguished from African ammoniacum. As, however, the latter is no longer in the market, it is probable that adulteration is at present out of the question, owing to the different origin of, and commercial channels traversed by, the two kinds; and, moreover, there is no risk of one being mistaken for the other, their external appearance being distinguishable at the first glance—quite apart from the analytical differences shown by Kremel and the author—although both give the umbelliferon reaction with hydrochloric acid and ammonia. (See above, detection of galbanum or African ammoniacum in Persian ammoniacum.)

Kremel obtained the following results—

| | Per cent. Resin. | Acid Value. (direct). | Ester Value. | Saponification Value (hot). |
|---|---|---|---|---|
| 1 Persian ammoniacum . | 67·7 | 112 | 30·6 | 142·6 |
| 2 Do. do. . | 67·1 | 110 | 50·0 | 160·0 |
| 3 Do. do. . | 70·7 | 100 | 50·5 | 150·5 |
| 4 African do. . | 77·6 | 59·0 | 123·0 | 182·0 |
| | | From extract. | | |

As stated in the introductory remarks, nearly all published values for ammoniacum have been obtained with extracts—the foregoing among them.

There being no difficulty in distinguishing between Persian and African ammoniacum, and between the latter and galbanum, by analytical means, the various unreliable qualitative colour reactions are, to say the least, superfluous.

E. Dieterich found—

| | | *Crudum.* | *Depuratum.* |
|---|---|---|---|
| From extract | Acid value (direct) . | 57·12–105·45 | 78·96–135·00 |
| | Ester value . . | 64·40– 91·22 | 73·00– 98·00 |
| | Sapon. value (hot) . | 146·16–196·67 | 180·00–233·00 |
| | Loss at 100° C. . . | 3·8 – 12·20 % | 2·15 % |
| | Ash . . . . | 0·9 – 10·08 % | 1·05– 2·75 % |

Solubility in—

| | | |
|---|---|---|
| Alcohol (96 per cent.), soluble | 46·0 – 88·20 % | 66·50–76·53 % |
| Do. do. insol. | 22·23– 42·96 % | — |

The acid, ester, and saponification values were determined by the same method as used by Kremel, but there is a much wider variation.

Beckurts and Brüche's determinations are as follows—

| No. | Commercial Variety. | Sp. gr. at 15° C. | Ash per cent. | Soluble in Alcohol per cent. | Acid Value (direct). | Ester Value. | Saponification Value (hot). |
|---|---|---|---|---|---|---|---|
| 1 | Depuratum | 1·214 | 4·47 | 59 | 69 | 37 | 106 |
| 2 | Do. | 1·198 | 3·20 | 63 | 75 | 22 | 97 |
| 3 | Do. | 1·190 | 0·79 | 68 | 80 | 19 | 99 |
| 4 | Do. | 1·200 | 3·97 | 61 | 76 | 38 | 114 |
| 5 | In granis | 1·200 | 3·84 | 56 | 70 | 35 | 105 |
| | | | | | From extract. | | |

The author has devised a method for examining ammoniacum, in which the crude product is used and not an extract; and the results obtained therewith give the first values actually referring to the unaltered crude product. The acid value is determined in one of two ways, either by the Reichert-Meissl method—distilling off the volatile matter—or by dissociating the ammoniacum, adding alkali, and titrating back in exactly five minutes. Direct titration is impracticable owing to the absence of a well-defined colour-change, the end point being masked by intermediate gradations of yellowish red. The operation of dissociating the crude drug with water and alcohol is necessary to dissolve out the acid constituents, thus rendering them accessible to the excess of alkali, which is left to act for only five minutes, since longer exposure would result in saponification. The total saponification value is found, together with the resin and gum values by fractional methods.

The *modus operandi* is as follows :—

(*a*) *Volatile acid value.*—One-half gr. of ammoniacum is mixed with a little water in a flask through which a current of steam is passed, the flask being placed on a heated sand bath to prevent excessive condensation of the steam. The receiver is charged with 40 c.c. of aqueous $\frac{n}{2}$

caustic potash, into which dips the tube leading from the condenser. Exactly 500 c.c. are distilled over, the inner tube of the condenser is well rinsed with distilled water, from the top downwards, and the liquid is titrated back in presence of phenolphthalein. The number of c.c. of KHO combined gives the volatile acid value when multiplied by 28·08.

"In this case, the volatile acid value expresses the number of mgrms. of KHO which 500 c.c. of distillate, obtained from 0·5 grm. of ammoniacum by steam distillation, are capable of combining."

(*b*) *Acid value* (indirect).—About one grm. of ammoniacum is boiled with 50 grms. of water for fifteen minutes, followed by 100 grms. of alcohol for an equal time, under a reflux condenser. After cooling, the weight is made up to 150 grms., and, after filtration, 75 grms. of filtrate (= 0·5 grm. of substance) are treated with 10 c.c. of alcoholic $\frac{n}{2}$ potash, left to stand for *exactly* five minutes, and then titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The volume (c.c.) of KHO combined, multiplied by 28·08 and referred to 1 grm. of substance, gives the acid value (indirect).

(*c*) *Resin value and gum value.*—Two samples (1 grm. each) of ammoniacum are employed, each being mixed with 50 c.c. of petroleum benzine (sp. gr. 0·700 at 15° C.), followed by 25 c.c. of alcoholic $\frac{n}{2}$ potash, and then left for twenty-four hours, at room temperature, in stoppered litre flasks, with frequent shaking. The one sample is then treated with 500 c.c. of water, and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein—this gives the "resin value." The second sample is treated with 25 c.c. of aqueous $\frac{n}{2}$ potash and 75 c.c. of water, and left, with frequent shakings, for another twenty-four hours, to be then diluted

with 500 c.c. of water, and titrated with $\frac{n}{2}$ sulphuric acid and phenolphthalein, accompanied by agitation. The result gives the "total saponification value."

The respective quantities (c.c.) of KHO consumed multiplied by 28·08 give the corresponding values.

The "gum value" is found by subtracting the resin value from the total saponification value.

(*d*) *Loss at* 100° C.—Two grms. of ammoniacum are dried in the oven at 100° C. until constant.

All values must be calculated to the unaltered crude drug.

(*e*) *Test for galbanum.*—Five grms. of the finely-ground ammoniacum are boiled in a small basin with 15 grms. of strong hydrochloric acid (sp. gr. 1·19) for fifteen minutes and filtered through a previously moistened, doubled filter. The clear filtrate is then carefully supersaturated with ammonia; whereupon, if galbanum be present, the liquid will exhibit, in reflected light, the characteristic blue fluorescence of umbelliferon.

The commercial varieties examined by the author gave the following results:—

| | |
|---|---|
| Volatile acid value | 100–200 |
| Acid value (indirect) | 90–105 |
| Resin value | 99·4 –155·4 |
| Gum value | 4·20– 46·2 |
| Total saponification value | 145·6 –162·4 |
| Loss at 100° C. | 2·15–12 per cent. |
| Ash | not over 10 „ |

The author has also applied the same method to adulterated samples, and found that in presence of adulterants the resin and total saponification values are diminished, as follows:—

| Ammoniacum with— | Resin Value. | Gum Value. | Total Sapon. Value. |
|---|---|---|---|
| 5 per cent. of Galbanum | 112·00 | 15·4 | 127·40 |
| 10 „ „ | 124·60 | 5·2 | 129·80 |
| 20 „ „ | 120·40 | 15·4 | 135·80 |

So far as the acid value is concerned, the estimation of the volatile acid is unsuitable for detecting adulteration; moreover, the method is a tedious one, and, like the Reichert-Meissl value methods for fats, requires a considerable amount of practice. On this account the author recommends the indirect acid value method as being more convenient and easier to perform. It should be stated that a good ammoniacum should show a high volatile acid value and resin value, but a low gum value.

The following values were furnished by African ammoniacum examined by the author's method :—

| | |
|---|---|
| Acid value (indirect) | 47·59– 92·21 |
| Resin value | 103·89–104·59 |
| Total saponification value | 105·30–108·10 |

The acid value (direct) in particular, of the African variety, fluctuates within rather wide limits, owing to the relatively considerable impurity of the drug. All the values are, in general, far lower than those given by Persian ammoniacum, and both the resin and the total saponification values are lower than in the case of galbanum (*q. v.*). A specimen of "ammoniacum depuratum" gave the acid value (ind.) 82·34–100.

Speaking generally, the author's method enables the crude drug to be used for analysis—bearing in mind the provisions laid down in the introductory remarks to this section—and also facilitates the accurate observation of the end-point in titration.

Mauch found that, similarly to other gum resins, ammoniacum is soluble in 60 per cent. chloral hydrate solution; and he recommends that, for determining the gum, the solution prepared with chloral hydrate (1–2 grms. in 10–15 grms.) should be filtered into 100 grms. of strong alcohol. By this means he obtained up to 21 per cent. of nearly pure gum.

Gregor found the methoxy value to be 8·6–9·0 and Bamberger 11.0.

(For the value of these tests, see *Chem. Rev.*, 1898, No. 10; and for the Germ. Pharm. tests for ammoniacum, see *Ph. C.*, 1898, No. 21.)

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## 43. Asafœtida.

*Gummi-resina asafœtida* (officinal in Germ. Pharm. III.).

**Origin and Habitat.**—*Ferula Scorodosma* and *F. Narthex*, Boiss. Persia.

**Chemical Constituents.**—Resin soluble in ether = ferulaic asaresinotannol ester, 61·4 per cent.; free asaresinotannol ($C_{24}H_{33}O_4OH$), 0·6 per cent.; gum, 25·1 per cent.; ethereal sulphurous oil, 6·7 per cent.; vanillin, 0·06 per cent.; free ferulaic acid ($C_{10}H_{10}O_4$), 1·28 per cent.; moisture, 2·36 per cent.; impurities, 2·5 per cent. (Polasek). Semmler

states that asafœtida contains pinene, another terpene in small amount and four di-sulphides, $C_7H_{14}S_2$, $C_{11}H_{20}S_2$, $C_{18}H_{18}S_2$, and $C_{10}H_{18}S_2$, besides an unidentified compound, $C_{10}H_{16}O$.

**General Properties and Commercial Varieties.**—The *in massa* and *in lacrymis* varieties of asafœtida are those now met with in commerce, the former being very impure, but the latter much purer. When fresh, the juice is white, though sometimes red or discoloured, with a strong smell of garlic; the external colour is dark violet, the flavour very sharp and persistently biting. As in the case of ammoniacum and galbanum, the variety *in massa* is preferable to the other for pharmaceutical purposes, on account of its higher percentage of ethereal oil.

The most inferior kind, *Asafœtida petræa*, or "petrified asafœtida," is a very impure mass, and should be rejected.

According to Dymock, three distinct kinds are recognised in the Bombay market, viz. *Abus ha heree* (from the port of Bunder Abbar, in the Persian Gulf), *Kanda haree*, and *Hingra*.

Whereas the first-named is derived from *Ferula alliacea*, Hingra is said to be the kind current in European commerce, the Persian asafœtida coming from *Scorodosma fœtidum*, and the Afghan from *Narthex Falconer*.

The very dear grade, "Hing from Abushaher" (in the province of Kerman), is said by Flückiger to be shipped in small quantities from Persian ports; and, according to Dymock, is adulterated with gum.

The present-day view, based on the researches of Holmes, is that all varieties presumably come from *Ferula Narthex*, Boiss.

**Adulterants.**—Inferior varieties, already exhausted by

extraction, and containing over 5 per cent. of ash; African ammoniacum; extraneous resins; and vegetable residues.

**Analysis.**—The following are old analyses of asafœtida—

| | Pelletier. | Brandes. |
|---|---|---|
| Resin | 65·00 | 48·85 |
| Gum | 19·44 | — |
| Gum with traces of saline matters | — | 19·40 |
| Bassorin | 11·66 | 6·40 |
| Volatile oil | 3·60 | 4·60 |
| Supermalate of lime | 0·30 | — |
| Extract with saline matters | — | 1·40 |
| $CaCO_3$, $CaSO_4$, $Fe_2O_3$, $Al_2O_3$ | — | 0·40 |
| Sand and lignin | — | 4·60 |
| Water | — | 6·00 |
| | 100·00 | 101·35 |

Asafœtida has been found to contain a larger percentage of ash and impurities than any other member of the gum resins. Waage stated that residues of the parent plant, etc., are frequently present; Muter described varieties containing up to 70 per cent. of stones; Evans' Sons, Lescher & Webb, in their *Analytical Notes*, record samples containing up to 69 per cent. of moderately large stones; samples containing 30 to 45 per cent. of ash are quite common; while Dymock mentioned the great frequency of intentional adulterations with sand, gum, etc. In view of the high ash content, E. Dieterich advised using the purified product, and showed that the percentage of ash can be reduced from 46 per cent. to 18 per cent., and the percentage soluble in alcohol increased from 29 per cent. to 57 per cent. On this point, however, the remarks already made in the introduction to the present section apply. Whereas the German Pharmacopœia fixes 6 per cent. as the maximum permissible percentage of ash,

the Dutch Pharmacopœia allows 20 per cent. of ash, the decision being based on the subjoined determinations :—

| | Ash per cent. |
|---|---|
| Asafœtida pulv. I[a]. . . . . | 53·75 |
| Do. in massa, extraf. . . . | 40·83 |
| Do. in massa . . . . . | 45·32 |
| Do. dep. pulv. . . . . | 50·43 |
| Do. in lacrymis . . . . | 2·08 |

Both the above limits appear to err, the Dutch on the side of leniency, the German on the side of stringency; and a medium course (10 per cent.) would be preferable.

J. N. Lloyd also occupied himself with the examination of asafœtida, his main attention being bestowed on adulterations with colophony or white turpentine, which are readily detected by their higher acid values. The samples examined, however, proved free from either admixture. The dry, hard drug " in tears " exhibits the highest acid value (61·9–68·2),[1] that of the semi-fluid kind being much lower (31·1–40·4). The ordinary commercial grade contains an enormous proportion of ash, the average being 16–20 per cent., and in individual instances attaining 50 per cent. The purest " tears," however, leave but very little ash (1·78–2·55 per cent.), and furnish about 76 per cent. of matters soluble in alcohol. It is stated that asafœtida *depurata* alone should be employed for officinal uses. Apparently it is almost impossible to find in the American market a quality complying with the requirements of the United States Pharmacopœia, which prescribes a 60 per cent. solubility in alcohol.

[1] These data do not justify the assumption that " tears " give a higher acid value generally than " mass," the contrary being usually the case with ammoniacum and galbanum, so that no general rule appears possible. See the results of Beckurts and Brüche (quoted later), in which the " tears " actually gave the lowest acid values.

Umney proposed the limit of ash allowable to be 15 per cent.

Morner and Fristedt detected a very subtle adulteration of asafœtida *in lacrymis*. Only 5 per cent. of the total drug was pure; whilst, of the remainder, 5 per cent. consisted of small fragments of gypsum, the rest being pieces of alabaster coated with a thin layer of asafœtida, the proportion of which varied from 7 per cent. in most of the lumps to 20 per cent. in others.

Hirschsohn examined numerous specimens, and found the following percentages soluble in petroleum ether :—

| | | Dried at 17° C. | at 120° C. |
|---|---|---|---|
| 1. | Asafœtida in granis . . | 8·25 | 3·27 |
| 2. | Do. do. . . | 5·33 | 2·12 |
| 3. | Do. do. . . | 1·85 | 1·02 |
| 4. | Do. in massis . . | 10·88 | 3·44 |
| 5. | Do. do. . . | 1·50 | 1·01 |
| 6. | Do. in granis . . | 7·40 | 1·73 |
| 7. | Do. petræa I. . . | 2·00 | 1·01 |
| 8. | Do. do. II. . . | 3·20 | 2·21 |
| 9. | Do. ordinary . . | 5·10 | 3·20 |
| 10. | Do. from Bombay . . | 11·44 | 4·65 |
| 11. | Do. from Hanbury . . | 13·45 | 3·44 |

He remarks: "The percentage soluble in petroleum ether should amount, in the case of an ordinary good commercial sample of asafœtida *in granis*, to at least 7 per cent., and to 5 per cent., at least, of the variety *in massis*. The quantity of matter volatilising at 120° C. should be not less than 5 per cent. and 3 per cent. respectively, referred to the total weight of the drug. A good quality of Indian asafœtida should yield not less than 11 per cent. to petroleum ether, and the residue should not lose less than 6 per cent. on being heated at 120° C."

Kremel, employing the ordinary method of examination, found—

| | | I. | II. |
|---|---|---|---|
| From extract | Resin per cent. | 72·1 | 35·6 |
| | Acid value (direct) | 26·8 | 54·8 |
| | Ester value | 145·2 | 182·1 |
| | Saponification value (hot) | 172·0 | 236·9 |

E. Dieterich found by the same method—

| | | Asafœtida. | |
|---|---|---|---|
| | | *Cruda.* | *Depurata.* |
| From extract | Acid value (direct) | 11·20– 55·00 | 23·52– 82·30 |
| | Ester value | 110·60–129·00 | 82·30–101·70 |
| | Saponification value (hot) | 121·80–184·00 | 164·60–171·70 |
| | Ash, per cent. | 6·5 – 66·05% | 1·60– 4·40% |
| | Sol. in 90 per cent. alcohol | 15·43– 59·66% | 66·00– 78·83% |

Beckurts and Brüche, also using the same method, obtained the following results:—

| Asafœtida. | Sp. gr. | Ash % | Soluble in Alcohol % | From extract | | |
|---|---|---|---|---|---|---|
| | | | | Acid Value (direct). | Ester Value. | Saponification Value (hot). |
| In massa | 1·730 | 1·2 | 36 | 40 | 141 | 181 |
| In depurata | 1·290 | 3·1 | 43 | 29 | 180 | 209 |
| | 1·280 | 2·9 | 50 | 31 | 183 | 214 |
| In massa | 1·293 | 5·0 | 58 | 43 | 162 | 205 |
| In granis | 1·316 | 5·8 | 44 | 27 | 179 | 206 |

and stated that the presence of turpentine can be reliably detected by the acid value.

As in the case of ammoniacum and galbanum, the present author has adopted a method for asafœtida which permits the use of the crude product instead of extract, and determines the acid value by back titration. This last-named process is applicable here, because asafœtida is difficult to saponify, cold or fractional saponification being impracticable. In back titration, the drug can be used direct without previous conversion into a solution or extract; and, moreover, the intermediate gradations of colour-change, which impede the reading of the end-point in direct titration, are here lacking.

The method is performed as follows:—

(*a*) *Acid value* (indirect).—One grm. of asafœtida is mixed with 10 c.c. each of alcoholic and aqueous $\frac{n}{2}$ potash, and left to stand in a stoppered glass flask for twenty-four hours at room temperature. After dilution with 500 c.c. of water, the whole is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein, the volume (c.c.) of KHO consumed multiplied by 28·08 giving the acid value.

(*b*) *Saponification value* (hot).—A 1 grm. average sample of the finely-triturated drug is mixed with 25 c.c. of alcoholic $\frac{n}{2}$ potash and boiled for one hour under a reflux condenser. At the end of that time 200 c.c. of alcohol are added, and, when cold, the whole is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The volume (c.c.) of consumed KHO multiplied by 28·08 gives the saponification value,

(*c*) *Ester value.*—Found by difference, as usual.

(*d*) *Ash determination.*—Two grms. of substance are carefully incinerated, and calcined until found constant after cooling in a desiccator.

The examination of a number of commercial samples furnished the author with the following values (in round figures):—

| | |
|---|---|
| Acid value (indirect) | 65– 80 |
| Ester value | 80–130 |
| Saponification value (hot) | 120–185 |
| Ash | 1– 10 per cent. |

Gregor and Bamberger obtained the following methoxyl values:—

| | I. | II. |
|---|---|---|
| Gregor | 11·9 | 6·9 |
| Bamberger | 18·0 | — |

Kitt found the carbonyl value = 0·2.

(For the value of these determinations see *Chem. Rev.*,

1898, No. 10; and for the Germ. Pharm. III. tests for asafœtida, see *Ph. C.*, 1899, No. 21.)

Mauch found that the gum and resin in asafœtida are soluble, forming a perfectly clear liquid in 10–15 parts of 60 per cent. chloral hydrate solution, and recommends this method for the detection of impurities. He says—

" This gum resin, often coming as it does into the market adulterated with sand, stones, etc., the estimation of the mineral constituents is rendered difficult. It is generally effected by incineration, as prescribed by the Germ. Pharm. III., the maximum permissible ash content being 6 per cent. Owing to the difficulty experienced in incinerating the gum resins, however, the determination may be made equally well, and with greater accuracy, by the aid of chloral hydrate, the drug being treated with 10–15 times its own weight of 60 per cent. chloral hydrate solution, whereupon all the gum and resin will slowly dissolve, leaving the mineral admixtures behind. The insoluble residue left is collected on a filter of known ash content, washed first with 60 per cent. chloral hydrate, and afterwards with a little alcohol, dried, calcined, and weighed."

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## 44. Bdellium.

*Gummi-resina Bdellium.*

**Origin and Habitat.**—African bdellium : *Commiphora Africana*[1] (Burseraceæ); East Indian bdellium : *Balsamodendron Indicum* (Burseraceæ). Senegal, East Indies.

**Chemical Constituents.**—Owing to the circumstance stated by Flückiger, that the experiments have been performed on specimens of doubtful origin—both African and Indian—the constituents cannot be given with certainty. Flückiger found the proportion of resin to be 70 per cent.; with small quantities of ethereal oil and gum, 29 per cent. According to Pelletier, African bdellium contains : resin, 59·0; soluble gum, 9·2; bassorin, 30·6; volatile oil and loss, 1·2.

**General Properties and Commercial Varieties.**—*East Indian bdellium* takes the form of agglomerated lumps of indeterminate shape about one inch in diameter, extremely dirty, resembling myrrh, and very impure. Externally they are rough, uneven, dull, and of dark brown colour, with a lustrous fracture, a sharp, bitter flavour, and an odour resembling Bisabol myrrh. With water the gum resin furnishes a whitish emulsion.

*African bdellium* is in reddish, oval or round lumps about half an inch across, which have a greasy lustre, and become soft and plastic when warmed. The gum resin gives with alcohol a golden yellow tincture, which is rendered turbid by water. Whereas a strip soaked in myrrh tincture and dried gives a bluish red coloration with nitric acid, this reaction does not occur in the case of bdellium (Berg).

As mentioned under Myrrh, bdellium does not yield the

[1] The real origin of bdellium is just as uncertain as that of myrrh. See Holmes' *Ph. Ztg.*, 1899, No. 28, p. 237, and P. Siedler, *Ap. Ztg.*, 1897, No. 2.

reaction with bromine vapour, besides which it differs analytically from both varieties of myrrh (see below). With regard to the origin and varieties of bdellium, Thiselton Dyer stated that this drug is exported from Berbera, a small port on the east coast of Africa, and is generally identified with the West African product on which the same name was bestowed by Guibourt. According to Royle, bdellium comes from *Balsamodendron Africanum*, Arnott, Guibourt being of the same opinion; descriptions are given by Dymock and Parker. Royle's *Materia Medica* contains a report, communicated by Johnston dealing with myrrh, in which it is stated that two varieties of the parent plant occur at Adel: the one, a low, thorny, ragged-looking tree, described by Ehrenberg, yielding the best commercial myrrh (*Balsamodendron myrrha*, or one of the forms of *B. opobalsamum*); the other, a tree rich in foliage, with coarsely serrated, dark green leaves, springing in fours or fives from a common centre, and with dried-up fruit berries, which is probably *B. Kua*. Thiselton Dyer is of opinion that *B. myrrha* furnishes myrrh, and *B. Kua*, African bdellium.

Opaque bdellium is described by Parker as opaque, ochreous yellow in colour, with a conchoidal fracture, very hard, inodorous, of bitter flavour, and often occurring in large, elliptical lumps with a granulated surface. It is shipped to India via Berbera. According to Dymock, opaque bdellium is often found in the bales of myrrh when these are sorted at Bombay; the drug is called "Meena harma," and is used as a remedy for the Guinea worm. According to the same author, opaque bdellium is of a yellowish white colour, similar to ammoniacum. Parker, however, regards Dymock's drug as the same gum resin which Vaughan names "Hotai." He states that the tincture from pure opaque bdellium gives an intense greenish black reaction with ferric

chloride, whereas the Hotai tincture does not. Parker regards *Balsamodendron Playfairii* as the origin of bdellium.

Dymock, in his Indian Pharmacognosis, describes two kinds of Indian bdellium. The one, from *Balsamodendron Mukul*, resembles the African drug in general, but is lighter, and often greenish in colour, with different odour and taste; many of the lumps are vermiform in shape, and as thick as the little finger. This kind is worth about one-third less than the African drug. The second kind comes from *B. Roxburghii*, and is in irregular lumps, more or less covered with dirt, bark, and hair; it is of a greenish yellow colour, with a tinge of red. The consistence is waxy, soft, and brittle, the odour peculiarly balsamic, recalling cedar wood, and the taste bitter. With water this grade forms a greenish white emulsion. It is not impossible that the two kinds are identical, and both derived from *B. Mukul*.

As even now, the published reports on the parent plants of myrrh, bdellium, and allied resins are still contradictory, any definite statement as to the origin of bdellium would be premature.

**Adulterants.**—Inorganic and vegetable impurities.

**Analysis.**—As already mentioned under Myrrh, the author has found bdellium give very low values in comparison with myrrhs; and it does not give the bromine reaction like Herabol myrrh.

Hirschsohn examined a number of specimens, and found the following percentages of matter soluble in petroleum ether :—

| | Dried at 17° C. | at 120° C. | |
|---|---|---|---|
| Bdellium Indicum . | 13·37 | 11·29 | Per cent. soluble. |
| Do. do. . | 16·57 | 9·87 | |
| Do. Africana . | 36·09 | 35·61 | |
| Do. do. . | 35·68 | 34·79 | |
| Do. do. . | 21·70 | 20·31 | |

According to these figures, petroleum ether dissolves out considerably more from the African varieties than from the Indian. (See also the analytical differences below.)

Kremel found—

74·3 per cent. of resin.

| | | |
|---|---|---|
| From extract | Acid value (direct) | 28·3 |
| | Ester value | 119·3 |
| | Saponification value (hot) | 147·6 |

Bdellium being a myrrh-like gum resin, the author has applied to it the same method of examination devised for myrrh, using the crude product instead of an extract (see p. 408).

*Percentage soluble in alcohol.*—Ten grms. of substance are extracted with strong (96 per cent.) alcohol, and the extract is dried at 100° C. until constant.

The author has obtained the subjoined results by this method:—

| | Acid Value (direct). | Ester Value. | Sapon. Value (hot). |
|---|---|---|---|
| African bdellium | 12·79 | 70·00 | 82·79 |
| | 14·43 | 69·33 | 83·76 |
| Do. do. | 9·73 | 96·39 | 106·12 |
| | 11·96 | 95·57 | 107·53 |
| Do. do. | 19·21 | 90·66 | 109·87 |
| | 20·81 | 90·14 | 110·95 |
| Indian do. | 35·69 | 46·75 | 82·44 |
| | 37·19 | 48·46 | 85·65 |

These values are quite as suitable for differentiating the two kinds, as is the percentage soluble in petroleum ether.

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## 45. Euphorbium.

*Gummi-resina Euphorbium* (officinal in Germ. Pharm. III.).

**Origin and Habitat.**—*Euphorbia resinifera* (Euphorbiaceæ). Morocco.

Other species of *Euphorbia*, such as *E. Cattimandoo*, *E. evemocorpus*, *E. pilulifera*, *E. helioscopia*, *E. geniculata*, *E. lathyris*, *E. Tirucalli*, also yield milky juices which contain euphorbon, are similar to euphorbium, and for the most part are utilised.

G. Henkel (*A. d. Ph.* 224, p. 729) examined numerous kinds of euphorbium, and his valuable work is worthy of special reference. He examined the drug from *E. resinifera*; *E. tetragona*; *E. Myrsinites*, L.; *E. orientalis*, L.; *E. virgata*, W.; *E. Lagascæ*, Spr.; *E. humifusa*, W.; *E. splendens*, B.; *E. Canariensis*; *E. fruiogona*; *E. nereifolia*; *E. virosa*; *E. palustris*; *E. Gerardiana*; *E. verrucosa*, L.; *E. exigua*, L.; *E. Cyparissias*, L.

**Chemical Constituents.**—Euphorbon ($C_{15}H_{24}O$, M.P. 113°–114° Hesse), 22 per cent.; gum, 18 per cent.; euphorbin ($C_{13}H_{22}O$, M.P. above 106°); caoutchouc; salts of malic acid; ash, 10 per cent.; amorphous acrid resin ($C_{10}H_{16}O_2$), 38 per cent. (Flückiger).

Pure euphorbium, divested of impurities, contains—euphorbon, 34·60 per cent.; resin soluble in ether, 26·95 per cent.; resin insoluble in ether, 14·25 per cent.; caoutchouc, 1·10 per cent.; malic acid, 1·50 per cent.; gum and salts insoluble in alcohol, 8·10 per cent.; gum and salts, not precipitated by alcohol, 12·30 per cent.; salts and organic matters soluble in ammonia, 1·20 per cent. (Henkel.)

Euphorbium, from *E. Cattimandoo*, exhibits similar constituents to that from *E. resinifera*—

Euphorbon, 35 per cent.; resin soluble in ether, 27·4

per cent.; resin insoluble in ether, 13·7 per cent.; caoutchouc, 1·5 per cent.; malic acid, 1·15 per cent.; gum and salts, insoluble in alcohol, 7·6 per cent.; gum and salts, not precipitated by alcohol, 12·15 per cent.; salts and organic matters, soluble in ammonia, 1·5 per cent. (Henkel.)

According to Tschirch and Paul, euphorbium contains 8 per cent. of ash, 96 per cent. alcohol dissolves 75 per cent., and water 32·5 per cent. It contains: euphorbic acid ($C_{24}H_{30}O_6$, M.P. 107°–108°), 0·7 per cent.; euphorbone ($C_{30}H_{40}O$, M.P. 115°–116°), 40 per cent.; euphorboresen ($C_{33}H_{43}O_4$, M.P. 74°–76°) and $\alpha$-euphorboresen ($C_{28}H_{48}O_4$, M.P. 75°) C, together 21 per cent.; calcium malate, 25 per cent.; carbohydrates, 2 per cent.; and impurities, etc., 11 per cent.

A sample of false euphorbium, described as "Gummi Euphorbium," was examined by A. Tschirch and Carl Leuchtenberger. This yielded $\psi$-euphorbone ($C_{15}H_{24}O_2$, M.P. 116°). Colourless crystals, $(a)_D + 48°{\cdot}18$, a substance closely related to euphorbone, and either an aldehyde or a ketone absorbing two atoms of iodine; $\psi$-euphorbic acid ($C_{24}H_{26}O_6$, M.P. 108°–109°); $\alpha$-$\psi$-euphorbonic acid ($C_{14}H_{22}O_{10}$, M.P. 112°–113°); $\beta$-$\psi$-euphorbonic acid ($C_{18}H_{28}O_{12}$, M.P. 81°), and $\psi$-euphorboresene ($C_{25}H_{64}O_{10}$, M.P. 54°–55°). In addition some calcium malate was found to be present.

**General Properties and Commercial Varieties.**—Readily pulverised, dull yellow lumps, enveloping the diacanthine leaf pads, the flower forks, and the three-lobed fruit. Euphorbium is slightly soluble in water, and almost completely so in alcohol. The taste is burning and acrid, and the powder induces sneezing. Sp. gr. 1·124.

**Adulterants.**—Inorganic and vegetable impurities.

**Analysis.**—Hirschsohn describes a kind of euphorbium,

from *E. resinifera*, which yielded 20 per cent. of constituents soluble in petroleum ether (dried at 120° C.). Euphorbium from *E. Tirucalli* gave 66·71 per cent.

According to Hirschsohn, this gum resin differs from ordinary euphorbium in being almost completely soluble in chloroform.

For the other kinds of euphorbium and their properties, see *A. d. Ph.* 224, pp. 729 *et seq.* (Henkel.)

Beckurts and Brüche made the following determinations :—

| | | I. | II. | III. |
|---|---|---|---|---|
| From extract | Acid value (direct) . . | 18 | 25 | 21 |
| | Ester value . . . | 63 | 68 | 49 |
| | Saponification value (hot) . | 81 | 93 | 70 |
| | Ash . . . . . | 2·0% | 1·8% | 1·3% |

They regarded the results as tentative, seeing that they were obtained from an insufficient number of specimens to permit of any conclusions being drawn therefrom.

Kremel found as follows :—

| | |
|---|---|
| Acid value (direct) . . . . . | 13·4 |
| Ester value . . . . . | 64·6 |
| Saponification value (hot) . . . . | 78·0 |

The author has devised the following method, based on the employment of the crude product instead of extracts, the saponification being effected by the fractional cold process, as in the case of other gum resins—

(*a*) *Acid value* (direct).—About one grm. of finely-pulverised euphorbium is treated with 100 c.c. of alcohol, warmed for fifteen minutes under a reflux condenser, and titrated, when cold, with alcoholic $\frac{n}{2}$ potash and phenolphthalein until the red colour-change appears. The number of c.c. consumed, referred to 1 grm. of substance, gives the acid value.

(*b*) *Resin and total saponification value.*—Duplicate 1 grm. samples are pulverised and treated, each with 50 c.c. of petroleum benzine (sp. gr. at 15° C. = 0·700) followed by 25 c.c. of alcoholic $\frac{n}{2}$ potash, the whole being then left in stoppered litre flasks for twenty-four hours at room temperature, with frequent shaking. The one sample is then diluted with 500 c.c. of water, and titrated back by agitating with $\frac{n}{2}$ sulphuric acid and phenolphthalein, the result giving the resin value. The second sample is treated subsequently with 25 c.c. of aqueous $\frac{n}{2}$ potash and 75 c.c. of water, and for a further period of twenty-four hours is submitted to frequent shaking. After dilution with 500 c.c. of water, the whole is titrated back by agitation with $\frac{n}{2}$ sulphuric acid and phenolphthalein, the result giving the total saponification value.

The respective volumes (c.c.) of KHO consumed multiplied by 28·08 give the corresponding values. The difference between the two is the "gum value."

The following values were obtained by the author :—

| | Acid Value (direct). | Resin Value. | Total Sapon. Value. | Gum Value. |
|---|---|---|---|---|
| 1. Euphorbium electum . | 13·4 | 71·40 | 85·40 | 14·00 |
| | | 71·40 | 88·20 | 16·80 |
| 2. Do. pulvis . | 25·0 | 77·00 | 86·80 | 9·80 |
| | | 72·80 | 85·40 | 12·60 |
| 3. Do. do. . | 21·00 | 72·10 | 82·60 | 10·50 |
| | | 72·80 | 85·40 | 12·60 |
| 4. Do. do. . | 19·60 | 77·00 | 89·60 | 12·60 |
| | | 78·40 | 91·00 | 12·60 |

Gregor and Bamberger found—

| | Methoxy Value— I. | II. |
|---|---|---|
| Gregor . . . . . | 0·0 | 2·8 |
| Bamberger . . . . . | 0·0 | 0·0 |

(For the value of these determinations, see *Chem. Rev.*, 1898, No. 10.) True analytical data for the scarcer varieties of euphorbium are altogether lacking.

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## 46. Galbanum.

*Gummi-resina Galbanum* (officinal in Germ. Pharm. III.).

**Origin and Habitat.**—*Peucedanum* (*Ferula*) *galbanifluum* and allied species (Umbelliferæ). Persia.

**Chemical Constituents.**—Ethereal oil, 9·5 per cent., containing *d*-pinene ($C_{10}H_{16}$) and cadinene ($C_{15}H_{24}$) (Wallach and Brühl), and oil ester (Conrady); resin soluble in alcohol, 63·5 per cent.; gum and impurities, 27 per cent. The pure resin contains combined umbelliferon ($C_9H_6O_3$), 20 per cent.; galbaresinotannol ($C_6H_{10}O$ or $C_{18}H_{29}O_2OH$), 50 per cent.; and free umbelliferon, 0·25 per cent. According to Conrady, the galbaresinotannol and umbelliferon are present as umbelliferon galbaresinotannol ester.

According to Aichison, a sample from Afghanistan contained :—

| | |
|---|---|
| Volatile oil . . . . . | 3·108 |
| Resin, soluble in ether . . . . | 61·200 |
| Do. do. alcohol . . . . | 7·576 |
| Gum, soluble in water . . . . | 17·028 |
| Insoluble matter . . . . . | 10·560 |

**General Properties and Commercial Varieties.**—The gum resin appears in the form of agglomerated tears or

masses, of wavy lustre and yellow or greenish colour. The *in massa* kind, consisting of agglomerated tears, is impure, but contains much ethereal oil, to which its greasy consistence is due. It is brown or dark brownish-yellow. The presence of the oil renders this kind particularly suitable for pharmaceutical purposes. The *in lacrymis* variety is purer, and in the form of grey globular masses which exhibit a white fracture, sp. gr. 1·212. The drug always contains vegetable fragments. The odour is strongly balsamic, the flavour bitter, sharp, and burning. Galbanum is but partially soluble in water, alcohol, and other solvents. When boiled with hydrochloric acid and supersaturated with ammonia, the filtrate exhibits the beautiful blue fluorescence of umbelliferon. When moistened with alcohol and addition of hydrochloric acid, it yields a purple colour (U.S. Pharm., 1880). According to Holmes, the so-called fluid Persian galbanum comes from a species allied to *Peucedanum galbanifluum*, and is to be met with in commerce at the present time; the consistence is about that of turpentine. The difference that formerly existed between Levantine galbanum (in tears and mass) and Persian galbanum (in mass and as a viscous fluid) can now be scarcely maintained; similar gum resins being furnished by different species of *Ferula*, and Persia being the main source of the supply. According to Holmes, all galbanum is Persian, even though the produce of different species; consequently the differences stated by Hirschsohn to exist between the Persian and Levantine gum resins appear dubious. Thomas has recently proposed Laretia resin, from *Laretia acaulis* (Umbelliferæ), which occurs in Chili, as a substitute for galbanum. The resin contains umbelliferon, and gives, in a slight degree, the hydrochloric acid reaction prescribed for galbanum in the German Pharmacopœia, though not the ammonia reaction.

**Adulterants.**—Inferior extracted galbanum, sand, fatty oils, Persian and African ammoniacum, turpentine.

**Analysis.**—Apart from the odour, galbanum is distinguishable from ammoniacum by the presence of umbelliferon, which may be detected by the reaction above mentioned, and differs in appearance from African ammoniacum, which also gives the umbelliferon reaction.

Hirschsohn examined several kinds of galbanum, and gave chemical methods of distinguishing between the Persian and Levantine gum resin; but, as already stated, these are no longer applicable. According to this authority, galbanum *in massa* should contain not less than 60 per cent. of matters soluble in petroleum ether (dried at 120° C.). Like Holmes, he also ascribed the fluid Persian galbanum to a separate species of *Ferula* or *Peucedanum*.

The following are old analyses of galbanum :—

| | Pelletier. |
|---|---|
| Resin | 66·86 |
| Gum | 19·28 |
| Volatile oil and loss | 6·34 |
| Wood, etc. | 7·52 |
| Supermalate of lime | traces |
| | 100·00 |

| | Meissner. |
|---|---|
| Resin | 65·8 |
| Gum | 22·6 |
| Bassorin | 1·8 |
| Volatile oil | 3·4 |
| Bitter matter with malic acid | 0·2 |
| Vegetable remains | 2·8 |
| Water | 2·0 |
| Loss | 1·4 |
| | 100·0 |

The figures obtained by Kremel are as follows :—

| | | I. | II. |
|---|---|---|---|
| | Resin, per cent. . . . | 74·3 | 74·2 |
| From extract | Acid value (direct) . . . | 28·3 | 28·3 |
| | Ester value . . . . | 119·3 | 132·2 |
| | Saponification value (hot) . . | 147·6 | 160·5 |

E. Dieterich found—

| | | *G. crudum.* | *G. depuratum.* |
|---|---|---|---|
| From extract | Acid value (direct) . . . | 5·16– 68·80 | 19·32– 46·26 |
| | Ester value . . . . | 82·10–179·00 | 55·70– 91·40 |
| | Saponification value (hot) . | 108·00–241·00 | 75·02–121·80 |
| | Loss at 100° C. . . . | 1·10– 30·98% | 8·61% |
| | Ash . . . . . | 0·45– 31·31% | 0·15– 2·10% |
| | Soluble in 90% alcohol . | 17·83– 71·50% | 45·60–92·16% |
| | Insoluble in 90% alcohol . | 45·58– 91·33% | 11·40–37·24% |
| | Water . . . . . | 21·40% | — |

This authority suggested that the gum resin should be purified, since the percentage of ash would be thereby reduced to about one-half. (See Introductory Remarks to this section.)

Conrady, who gave considerable attention to galbanum, and may be regarded as a true connoisseur, states as follows :—

" My observations on the ash content, etc., fully coincide with the reports of E. Dieterich. With regard to the lower acid and ester values of galbanum this is readily explainable, seeing that, according to a private communication, the ethereal oil is first driven over with steam, and with it the free fatty acids, therefore, taking into account the difficult saponification of galbanum, the liquid esters which are saponified by this treatment can alone be in question. The distillation could of course be easily dispensed with, and replaced by cold extraction with petroleum ether, the unsaponified oil being then returned to the purified resin. In such case the *Galbanum depuratum* would really merit that

title, and meet all the requirements of the Pharmacopœia; for one was able to detect both the free umbelliferon and also that combined by saponification after this treatment. The purified galbanum also gives the same hydrochloric acid reaction as the crude drug, on which account a portion of the oil is probably not fully saponified.

"The lowering of the ester value is the sole noticeable difference from crude galbanum, and therefore a minimum ester value of 130 might be required of all galbanum. It is necessary, however, that, as already laid down by Lüdy for benzoin, an exact limit of time for the saponification process should be fixed. It would be still better, in the case of galbanum, to saponify it by the aid of steam, and titrate the distillate direct; this would mean that only the acid from the liquid esters would be titrated—the advantage of this being to facilitate the fixing of a standard for the acid and ester values within narrow limits, owing to the slight fluctuation in the percentage of ethereal oil exhibited by the current commercial varieties of the drug."

Subsequently it was shown by the author that the determination of the acid value, as advocated by Conrady, cannot be affected so simply, but requires special precautions. Furthermore, the author has shown that the method of determining the acid value, based on the Reichert-Meissl principle, is tedious, and requires much practice. On this point more will be said later.

Beckurts and Brüche found the following:—

| | Sp. gr. at 15° C. | Ash % | Soluble in Alcohol % | From extract | | |
|---|---|---|---|---|---|---|
| | | | | Acid Value (direct). | Ester Value. | Saponification Value (hot). |
| 1. G. depur | 1·110 | 4·0 | 63 | 22 | 82 | 104 |
| 2. Do. | 1·130 | 8·7 | 56 | 19 | 91 | 110 |
| 3. Do. | 1·109 | 4·1 | 58 | 40 | 69 | 109 |
| 4. Do. | 1·133 | 8·4 | 54 | 19 | 63 | 82 |
| 5. G. in granis | 1·121 | 4·9 | 60 | 25 | 90 | 115 |

The authors noted that the ash content is in direct ratio to the sp. gr., so that galbanum with the highest sp. gr. also exhibits the largest percentage of ash. In addition, they recommend the acid, ester, and saponification values as data for detecting adulteration, without, however, giving any results obtained by them.

The present author has worked out a new method for galbanum, and examined a large number of kinds, the results showing that Conrady's proposal for determining the acid value is impracticable; the use of alkali in the receiver being necessary to prevent loss.

As this method is nevertheless tedious, and entails much practice, the author applied to galbanum the same convenient method he used for ammoniacum (see p. 362), the gum resin being saponified, and then titrated back, for the same reasons as with ammoniacum. The resin, gum, and total saponification values are determined by the cold fractionation method. The author's method presents the advantages of furnishing liquids easily titrated, enabling the crude product to be used—not extracts—and giving concordant values, so far as these can *à priori* be expected from gum resins.

The following limits of value were obtained by the author from a large number of specimens:—

| | |
|---|---|
| Volatile acid value | 73·5 –114·0 |
| Acid value | 21·24– 63·45 |
| Resin value | 107·5 –122·5 |
| Total saponification value | 116·2 –135·8 |
| Gum value | 8·4 – 16·1 |
| Ash | 1–10 per cent. |
| Loss at 100° C. | 0·35–31·5 ,, |

Further analyses performed by the author show that, contrary to the opinion of Beckurts and Brüche, the ester, and saponification values, or resin, total saponification, and

gum values are not suitable for detecting adulteration, though the acid values are of use in both methods.

The results obtained are subjoined :—

| | Galbanum with— | Volatile Acid Value. | Average. | Acid Value (indirect). |
|---|---|---|---|---|
| 1. | 5% of ammoniacum | 75·60– 83·44 | 75·52 | 29·00–37·68 |
| 2. | 10% do. | 70·00– 79·52 | 74·67 | 33·00–47·00 |
| 3. | 20% do. | 59·92– 64·40 | 62·16 | 42·34–66·51 |
| 4. | 5% of asafœtida | 105·00–117·60 | 111·30 | 34·77–46·13 |
| 5. | 10% do. | 119·28–120·96 | 120·12 | 29·84–36·66 |
| 6. | 20% do. | detectable by the odour, as were also 4 and 5. | | 21·45–29·87 |

From these figures it is evident that adulteration with ammoniacum decreases the volatile acid value, whereas asafœtida has the reverse effect. Even as low as 5 per cent. of asafœtida is revealed by its penetrating smell observed during the distillation. On the other hand, the indirect acid value is raised by ammoniacum (which has a higher acid value), but is reduced by asafœtida.

Neglecting the qualitative reactions of Picards and Plugge, the quantitative acid values just mentioned are to be recommended for this purpose.

The high percentage of ash—30 per cent.—is, of course, abnormal, 10 per cent. being the maximum that a good galbanum should exhibit—as expressed by the Swiss Pharmacopœia, which prescribes 8 per cent. of ash as the highest limit. No mention is made of ash content in the German Pharmacopœia.

Evans' obtained the following figures with commercial samples of galbanum :—

| | |
|---|---|
| Ash | 3·7– 6·0 per cent. |
| Insoluble in 90 per cent. alcohol | 29·8–31·0 „ |

Portion soluble in alcohol :—

| | |
|---|---|
| Acid value (direct) | 9·8– 13·0 |
| Saponification value | 137·3–162·9 |
| Iodine value | 34·6– 90 |

Gregor and Bamberger found—

| | Methoxyl Value |
|---|---|
| Gregor . . . . . | 3·7 |
| Bamberger . . . . . | 3·7 |

The importance of these values is criticised in *Chem. Rev.*, 1898, No. 10; and the Germ. Pharm. III. tests for galbanum in *Ph. C.*, 1898, No. 21. Finally, it may be mentioned that, according to Mauch, galbanum dissolves in 67 per cent. chloral hydrate, forming a yellow liquid, which is rendered milky by water and turbid by alcohol, gum being deposited. The umbelliferon reaction is also furnished by this solution.

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## 47. Gamboge.

*Gummi-Resina Gutti* (officinal in Germ. Pharm. III.).

**Origin and Habitat.** — *Garcinia Morella*, *D.* (*G. Hanburii*), (Clusiaceæ). Siam, Ceylon.

**Chemical Constituents.**—Gum, 13·8 per cent., resin, gambogic acid ($C_{30}H_{35}O_6$, M.P. 75°–80°), 70 per cent., wax and ash, vegetable detritus; no ethereal oil. (Gum 26 per cent., resin 66 per cent.) The gum, although soluble in water, is, according to Flückiger, not the same as gum arabic. According to Sassarini, gamboge contains gum analogous

to arabin, volatile oil consisting of a terpene and camphor, isouvitinic acid, acetic acid, a phenol ester, resin, methyl alcohol and its homologues, and an aldehyde or ketone.

**General Properties and Commercial Varieties.**—Gamboge comes into the market in the form of pipes, up to three inches thick; also cakes or lumps, of reddish yellow colour covered with a yellow powder and large conchoid lustrous fracture, specific gravity 1·221. At 20° C. they float in carbon di-sulphide, but sink at higher temperatures; and they furnish a yellow emulsion with water. The mass is plastic at 100° C.; it is only partially soluble in water, alcohol, and ether, and the solution has an acid reaction. The pipe forms are the best, then the cakes, and lastly, the mass form. There are two chief commercial varieties—Siam gamboge and Ceylon gamboge, but the latter is rare.

**Adulterants.**—Vegetable impurities, rice meal, sand, dirt, starch, dextrin, and colophony; the last-named, in particular, being used to adulterate the powder.

**Analysis.**—Gamboge has been frequently analysed. Williams, for instance, found—

| | |
|---|---|
| Acid value (direct) | 80·6 |
| Ester value | 67·2 |
| Saponification value (hot) | 147·8 |
| Iodine value | 115·8 |
| Ash | 0·48 per cent. |
| Moisture | 3·70 ,, |

Costelo exhausted 10 grms. of various samples, with alcohol, and found—

| | | Resin. | Gum. | Impurities. | Total. |
|---|---|---|---|---|---|
| Gamboge in | Lump | 6·76 | 2·74 | 0·38 | 9·88 |
| | Pipes | 7·93 | 1·94 | 0·15 | 9·89 |
| | Powder | 7·66 | 2·25 | 0·07 | 9·98 |

the balance being moisture.

D. Hooper has examined a sample of gamboge, the product of *G. Cowa*, from Chittagong and found it to be richer in resin than the ordinary varieties, the figures being: Resin, 84·3; gum, 5·6; mineral matter, 1·1; moisture, 6·5; and insoluble matter, 2·5 per cent. The gum resin was paler in colour than the ordinary commercial kinds of gamboge. Hirst has also examined the ordinary gamboge of commerce, with the following results: resin (soluble in ether), 66·05; wax (soluble in alcohol), 4·31; gum, 26·03; mineral matter, 1·05; and moisture, 2·50 per cent.

Appended are a number of results by Christison :—

| | Resin. | Gum. | Amylaceous Matter. | Wood Fibre. | Moisture. |
|---|---|---|---|---|---|
| Pipe gamboge from Siam . | 74·2 | 21·8 | — | — | 4·8 |
| ,, ,, ,, ,, . | 71·6 | 24·0 | — | — | 4·8 |
| Cake ,, ,, ,, . | 64·3 | 20·7 | 6·2 | 4·4 | 4·0 |
| ,, ,, ,, ,, . | 65·0 | 19·7 | 5·0 | 6·2 | 4·6 |
| Gamboge from Ceylon . | 68·8 | 20·7 | — | 6·8 | 4·6 |
| ,, ,, ,, . | 71·5 | 18·8 | — | 5·7 | — |
| ,, ,, ,, . | 72·9 | 19·4 | — | 4·3 | — |
| ,, ,, ,, . | 75·5 | 18·4 | — | 0·6 | — |

A sample of Garcinia resin, from a species found at Perak, in the Federated Malay States, not yet identified, has been examined at the laboratories of the Imperial Institute. This is stated to be formed from the sap by boiling. It does not resemble the ordinary gamboge from *Garcinia Hanburii* or *G. morella*, but forms a soft opaque mass smelling somewhat like tung oil, and covered with a brittle coating which is insoluble in turpentine, etc. The soft resin dissolves completely in turpentine, chloroform, benzene, and ether, and is almost entirely dissolved by alcohol. Its acid value is 89·2 and saponification value 93·5; ash 0·21 per cent. and melting point 65°.

Von Schmidt and Erban found the solubility to be in—

| | |
|---|---|
| Alcohol<br>Ether<br>Methyl alcohol<br>Amyl alcohol<br>Benzol<br>Petroleum ether<br>Acetone<br>Glacial acetic acid<br>Chloroform<br>Carbon di-sulphide<br>Oil of turpentine | partly soluble. |

| | | |
|---|---|---|
| From extract | Acid value (direct) . . | 80·3 |
| | Ester value . . . | not examined. |
| | Saponification value . . | |

The foregoing values, being obtained from an extract, are of merely relative value in forming an opinion.

A. Kremel found—

| | | |
|---|---|---|
| | Resin . . . . . | 79·6 per cent. |
| From extract | Acid value (direct) . . . | 100·0 ,, |
| | Ester value . . . . | 56·7 ,, |
| | Saponification value (hot) . . | 156·7 ,, |

Kremel's figures also were obtained from extracts, and their value is therefore only relative.

Beckurts and Brüche also obtained the following results:—

| | | I. | II. | III. | IV. |
|---|---|---|---|---|---|
| | Ash, per cent. . . | 0·49 | 0·63 | 0·58 | 0·71 |
| From extract | Acid value (direct) . . | 89 | 81 | 69 | 71 |
| | Ester value . . . | 61 | 50 | 43 | 44 |
| | Saponification value (hot) | 150 | 131 | 112 | 115 |

The remarks made on Kremel's values also apply here.

Mills and Muter found saponification value 155 and bromine value 71·6.

As the best neutral solvent for gamboge the author recommends: strong alcohol, 2 parts; water, 1 part,—used in succession, not in admixture. The acid value (direct), resin, total saponification, and gum values of the natural drug—not extract—(see fractional saponification in Part I.) have been obtained by the following methods :—

(*a*) *Acid value, direct.*—One grm. of the finely triturated natural gamboge is warmed with 100 grms. of alcohol under a reflux condenser for fifteen minutes, 50 grms. of water being added, and the whole left to stand until as much as possible has been dissolved. When quite cold, the liquid is titrated with alcoholic $\frac{n}{2}$ caustic potash until the added drops of alkali no longer turn red, but the whole liquid assumes a red coloration.

(*b*) *Resin value and total saponification value.*—Two 1 grm. samples of finely triturated gamboge—taken as average samples of a larger quantity—are each mixed with 25 c.c. of alcoholic $\frac{n}{2}$ potash, and are left for twenty-four hours in tightly stoppered flasks. The one sample is then diluted with water and titrated, the volume (c.c.) of KHO consumed multiplied by 28·08 giving the resin value. The second sample receives an addition of 25 c.c. of aqueous $\frac{n}{2}$ potash, and is titrated back after standing twenty-four hours longer, the result giving the total saponification value. The gum value is obtained by difference.

This method enables the natural drug to be used, and also furnishes a readily detectable colour-change at the end-point. The preliminary dissolution with alcohol and water, in the proportion of 2 to 1 for the acid value determination, gives an almost complete solution easily titrated.

The author obtained the following values :—

Natural gamboge (pipes) :

Acid value (direct). 1. 71·45 5. 86·46
2. 78·60 6. 83 60
3. 79·31 7. 84·31
4. 85·03

| | Resin Value. | Total Sapon. Value. | Gum Value. |
|---|---|---|---|
| 1. Gamboge, *naturale* . . | 109·20 | 127·40 | 18·20 |
| | 110·60 | 131·60 | 21·00 |
| 2. Do. *pulvis* . . | 110·60 | 124·60 | 14·00 |
| | 112·00 | 133·00 | 21·00 |
| 3. Do. *naturale* . . | 105·00 | 121·80 | 16·80 |
| | 107·80 | 124·60 | 16·80 |
| 4. Do. *do.* . . | 110·60 | 128·80 | 18·20 |
| | 110·60 | 128·80 | 18·20 |
| 5. Do. *electum* . . | 114·80 | 137·20 | 22·40 |
| | 116·20 | 138·60 | 22·40 |

The "pulvis" variety seems, like nearly all resins in powder, to be adulterated with colophony.

A further noteworthy contribution on the testing of gamboge is supplied by Eberhardt, who examined more particularly for starch.

He proceeds as follows :—

One grm. of the powder to be tested is dissolved in 5 c.c. of potash solution, followed by an addition of 45 c.c. of water, and finally slight excess of hydrochloric acid. The turbid liquid is then filtered through cotton-wool, and one or two drops of iodine are added to the clear filtrate. In presence of over 2 per cent. of starch there immediately ensues a dark blue coloration, or a similarly coloured precipitate is formed. The powdered commercial drug usually gives a yellow coloration, which afterwards turns blue; pure gamboge, with 1 per cent. of added starch, gives a dull blue,

which deepens on standing, and deposits a precipitate after several hours. Five to ten per cent. of starch gives a blue precipitate immediately. Five per cent. and under of turmeric also gives decided starch reactions. If a precipitate be obtained at once, adulteration may be assumed, though sometimes adulterants are present when the drug is free from starch, in which event the resin determination is the best test. Eberhardt determined the resin content in several specimens free from starch by dissolving in alcohol, and found 75·9–81·4 per cent. soluble, with 18·6–24·1 per cent. of residue.

Woolsey also reports on adulterated gamboge, and lays down the minimum resin content as 70–80 per cent., with 3–4 per cent. as the maximum for ash, and 4–6 per cent. of moisture.

According to Mauch, gamboge is soluble in five parts of a 60 per cent. solution of chloral hydrate. If the gum be determined by precipitation with alcohol, a very pure product, amounting to 16 per cent., is obtained (Mauch). The method is also applicable to the detection of impurities (see Asafœtida).

Kitt determined the carbonyl value of gamboge to be 1·25–1·38.

Gregor and Bamberger have also examined the methoxyl value, and found—

| | Methoxyl Value. | |
|---|---|---|
| Gregor . . . . . | 3·7 | 0·0 |
| Bamberger . . . . . | 3·7 | 0·0 |

(For the value of these determinations, see *Chem. Rev.*, 1898, No. 10; and for the Germ. Pharmacopœia tests, see the author's remarks in *Ph. C.*, 1898, No. 21.)

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**Gum Resin of Kaya Madagascariensis.**—This tree, belonging to the *Meliaceæ*, yields a resinous exudation product which has the characters of a gum resin. On treatment with water 54·8 per cent. dissolves. This consists of a gum resembling gum arabic but which is dextrorotatory. On hydrolysis it yields galactose and pentoses, and it contains enzymes, including an oxidase, a peroxidase, an emulsin, but no myrosin.

## 48. Lactucarium.

*Lactucarium Germanicum.*

**Origin and Habitat.**—*Lactuca virosa*, L. (Compositæ). Europe.

**Chemical Constituents.**—Lactucin (crystalline, bitter principle), $C_{11}H_{14}O$; lactucic acid (bitter and crystalline) (Kromayer); lactucon (neutral and crystalline), $C_{15}H_{24}O$ (Ludwig) or $C_{19}H_{30}O$ (O. Schmidt); asparagin (?); caoutchouc; ash, 10 per cent.; mannite (?). English lactucarium is of similar composition, there being no appreciable divergences.

**General Properties and Commercial Varieties.**—*Lactucarium Germanicum* forms tough, homogeneous, yellow-brown masses, somewhat waxy in fracture and hygroscopic. The taste is irritant, bitter, and narcotic. It is only partially soluble in water, ether, and alcohol.

*Lactucarium Anglicum*, which is also derived from *Lactuca virosa*, consists of irregular, large and smaller granules, more or less obtuse angled, dull, friable, dark brown in colour, and non-hygroscopic.

*Lactucarium Gallicum*, the "Thridax" of the ancients, comes from *Lactuca sativa*, and forms a fatty extract, blackish brown in colour. A lactucarium is also furnished by *L. Canadensis*.

**Adulterants.**—Inferior vegetable extracts, and various kinds of bread.

**Analysis.**—No true analytical data on the German variety are available.

Hanausek reported upon an imitation lactucarium, consisting of brown granules of various sizes, devoid of odour or flavour, and then swelling up in water, falling into smaller granules. The examination showed that this product consisted of old wheaten bread.

Kremel found an admixture of bread crumbs in various specimens of lactucarium, the adulteration being capable of detection by both chemical and microscopical means. If lactucarium be treated in an extractor, with 3 parts of alcohol and 1 of chloroform, lactucon is the chief constituent dissolved, the extract amounting to from 55–69 per cent. in the case of the pure drug. When an admixture of bread is present, the percentage of extract is proportionally lower, and the percentages of moisture and ash are also effected thereby. The following analyses of three kinds of lactucarium may serve as examples :—

| | Moisture % | Ash % | Chloroform-alcohol Extract % |
|---|---|---|---|
| I. | 5·80 | 6·50 | 57·46 |
| II. | 5·88 | 4·51 | 40·00 |
| III. | 10·84 | 1·61 | 11·54 |

No. I. was pure *Lactucarium Germanicum*; Nos. II. and III., adulterated *L. Austriacum*. Swollen starch granules could be detected in the two latter under the microscope, and a blue coloration was furnished on testing a boiled sample with iodine, when cold.

According to Kremel, lactucarium yields at least 50 per cent. of matters soluble in a mixture of 3 parts of alcohol and 1 of chloroform.

The author has examined German and English lactucarium, and determined the resin and total saponification values by fractional saponification, according to the following method :—

Two 1 grm. samples of lactucarium are triturated, and each mixed with 50 c.c. of petroleum benzine (sp. gr. 0·700), followed by 25 c.c. of alcoholic $\frac{n}{2}$ potash, the whole being left to stand in the cold for twenty-four hours in stoppered litre flasks, with frequent shaking. The one sample is then diluted with 500 c.c. of water, and at once titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein, by agitation, the results giving the resin value. The second sample is further treated with 25 c.c. of aqueous $\frac{n}{2}$ potash and 75 grms. of water, and is left for another twenty-four hours, with frequent shaking, at the end of which time it is diluted with 500 c.c. of water and titrated back by $\frac{n}{2}$ sulphuric acid and phenolphthalein, with agitation. The resulting figures represent the "total saponification value," the gum value being ascertained by difference.

The author obtained the following values :—

| | | Resin Value. | Total Sapon. Value. | Gum Value. |
|---|---|---|---|---|
| 1. | Lactucarium Germanicum pulvis | 203·00 | 215·60 | 12·60 |
| | | 207·20 | 217·00 | 9·80 |
| 2. | Do. do. in massa | 154·00 | 166·60 | 12·60 |
| | | 156·80 | 169·40 | 12·60 |
| 3. | Do. do. pulvis | 189·00 | 191·80 | 2·80 |
| | | 191·80 | 191·80 | 0·00 |
| 4. | Do. do. do. | 249·20 | 310·80 | 61·60 |
| | | 252·00 | 313·60 | 61·60 |
| 5. | Do. | 163·80 | 190·40 | 26·60 |
| | | 162·40 | 184·80 | 22·40 |
| 6. | Do. Anglicum . . | 68·60 | 75·60 | 7·00 |
| | | 67·20 | 75·60 | 8·40 |
| 7. | Do. do. . . | 225·40 | 232·40 | 7·00 |
| | | 225·40 | 238·00 | 12·60 |
| 8. | Do. do. . . | 50·40 | 75·60 | 25·20 |
| | | 51·80 | 78·40 | 26·60 |

Whereas the figures obtained with German lactucarium fluctuate within relatively narrow limits—when the two classes " pulvis " and " massa " are considered by themselves —those furnished by the English drug indicate very irregular composition. As in the case of nearly all resinous products, the " pulvis " varieties of German lactucarium gave the highest values, so that here also an adulteration with colophony may be assumed (see conclusion to Part I.).

(For the detection of colophony, by the Storch-Morawski reaction, see under Colophony.)

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## 49. Myrrh.

*Gummi-resina Myrrha* (*Herabol Myrrh* officinal in German Pharmacopœia III.).

The following are old analyses of Myrrh :—

| | Pelletier, 1816. | Brandes, 1819. | Braconot, 1819. |
|---|---|---|---|
| Volatile oil | | 2·60 | 2·50 |
| Resin { soft / hard } | 34 | 22·24 / 5·56 | 23·0 |
| Gum { soluble / insoluble } | 66 | 54·38 / 9·32 | 46·0 / 12·0 |
| Salts (benzoates, malates, phosphates, sulphates and acetates of potash and lime) | — | 1·36 | — |
| Impurities | — | 1·60 | — |
| Loss or undetermined | — | 2·94 | 16·5 |
| | 100 | 100·00 | 100·0 |

Ruickoldt obtained the following results :—

| | |
|---|---|
| Volatile oil | 2·183 |
| Resin | 44·760 |
| Gum or Arabin | 40·818 |
| Water | 1·475 |
| Calcium and Magnesium carbonates | 3·650 |
| Traces of $CaSO_4$ and $Fe_2O_3$. | |
| | 92·886 |

I. Herabol Myrrh (the usual commercial grade).

**Origin and Habitat.**[1]—Species of *Balsamodendron* and *Commiphora* (Burseraceæ). Arabia.

[1] In spite of numerous researches, the conflicting views published on the origin of myrrh, bdellium, and similar bodies have not yet been fully settled. Consequently, any definite statement would be premature. On this point, see Holmes, *Ph. Ztg.*, 1899, pp. 237–238, and P. Siedler, *Ap. Ztg.*, 1898, No. 2.

**Chemical Constituents.**—Gum 57–59 per cent., 8·4 per cent. insoluble in water; resin; and ethereal oil. The first-named corresponds to the formula $C_6H_{10}O_5$. The portion readily soluble in alcohol is a mixture of various resins: a neutral resene, and a soft resin (soluble in alcohol) of the formula $C_{26}H_{34}O_5$, with three hydroxyl groups, and two resin acids. Both the latter are dibasic, one having the formula $C_{13}H_{16}O_8$ ($C_{26}H_{34}O_5$); the other, the formula $C_{26}H_{32}O_9$. Ethereal oil—myrrhol or myrrhenol—7–8 per cent., the chief constituent of which has the formula $C_{10}H_{14}O$, and is isomeric with thymol and carvacrol. (Ruickoldt, O. Köhler.) The volatile oil had a sp. gr. of 1·0189 at 7·5°, boiling point 266°, and was lævorotatory. The resin or myrrhin ($C_{38}H_{32}O_{10}$) is neutral but becomes acid after heating for a time (Gladstone).

From a commercial sample of Herabol myrrh, O. von Friedrichs has isolated and identified a very large number of constituents. By steam distillation it yielded a thick yellowish volatile oil, sp. gr. 1·011, refractive index at 20° 1·5359, and optical rotation $[a]_D$ −73·9 at 20°. This oil had an acid number 6·15 and ester number 47·6, and contained formic and acetic acids, also a crystalline acid, M.P. 159°, *m*-cresol, cuminaldehyde, cinnamaldehyde, and a crystalline monobasic acid (myrrholic acid $C_{17}H_{22}O_5$, M.P. 236°), also a sesquiterpene-heerabolene ($C_{15}H_{24}$, B.P. 130°–136°) at 16 mm. pressure, sp. gr. at 20°, 0·943, refractive index at 20°, 1·5125, and optical rotation at 20°, 14°–10′ in 100 mm. tube.

The resin contained *α*-commiphoric acid ($C_{14}H_{18}O_4$, M.P. 201–203°); *β*-commiphoric acid ($C_{14}H_{18}O_4$, M.P. 205°); *γ*-commiphoric acid ($C_{17}H_{22}O_5$, M.P. 169°–172°); commiphorinic acid ($C_{28}H_{36}O_8$, M.P. 135°); *α*-heerabo-myrrholic acid ($C_{15}H_{22}O_7$, M.P. 220°–225°); *β*-myrrholic acid ($C_{25}H_{32}O_6$, M.P. 187°–190°); *α*-heerabo-myrrhol ($C_{18}H_{26}O_5$, M.P. 248°–

250°); $\beta$-heerabo-myrrhol ($C_{20}H_{26}O_4$, M.P. 168°). A yellow alcohol ($C_{14}H_{22}O_2$, B.P. 264°); and heeraboresene ($C_{42}H_{56}O_8$, M.P. 100°–102°). The gum had a rotation $[\alpha]_D$ + 23·8° in 2 per cent. solution and contained an oxydase. It also contained both galactan and araban.

**General Properties.**—Myrrh occurs in the form of masses or granules as large as a nut, yellowish red in colour, with a greasy, lustrous, fine-grained fracture, not smooth or conchoid, usually covered with a fine powder or dust. (sp. gr. 1·36). Water produces with it a white emulsion; alcohol dissolves only the resin. The odour is strong, and the taste persistently bitter and irritant. Herabol myrrh is the so-called "male myrrh."

**Adulterants.**—Extracted myrrh resin, bdellium, gum arabic, Bisabol myrrh.

### II. Bisabol Myrrh.

**Origin and Habitat.**—(See note to Herabol myrrh.) *Balsamea erythrea*, Engl. (Burseraceæ). Somaliland.

**Chemical Constituents.**—Gum soluble in water, 22·1 per cent.; gum soluble in caustic soda, 29·85 per cent.; crude resin, 21·5 per cent.; bitter principle, 1·5 per cent.; ethereal oil (sp. gr. 0·8836, B.P. 220°–270°), 7·8 per cent.; water, 3·17 per cent.; vegetable detritus, 13·4 per cent. The ethereal oil contains a hydrocarbon, bisabolene, of the formula $C_{10}H_{16}$, B.P. 259°–260° C., also ester-like compounds and an oxygenated body ($C_{56}H_{96}O$), corresponding to a double molecule of chironol ($C_{28}H_{48}O$), minus one atom of oxygen (see Opopanax). The pure resin contains two free acids and two combined acids, one being $C_9H_{13}O_2$, a resene (Bisabol resene, $C_{29}H_{47}O_6$), and a neutral substance. (Tucholka.)

**General Properties and Commercial Varieties.**—Similar to Herabol myrrh, but with a milder and weaker

taste and with an odour more like that of bdellium. This Bisabol myrrh is known as " female myrrh."

**Adulterants, etc.**—Bisabol myrrh can only be confounded with Herabol myrrh. It is generally consumed in the producing countries, and is rarely met with in commerce.

Other kinds of myrrh, such as Arabian, Meetiya, Persian, and Chinaïbol (Siam) myrrh, are of interest to the producing countries exclusively, and not to the European trade. Hooper recommends as an excellent substitute for myrrh, the gum resin from *Balsamodendron Berryi*, known as *Mulukilivary* in its East Indian habitat. This myrrh contains 84 per cent. of gum, 5 per cent. of water, and 6·6 per cent. of mineral matter. The gum is not precipitable by lead acetate, thus differing from the gum in ordinary myrrh; the soft resin is dextrorotatory, and is soluble in ether, alcohol, chloroform, and carbon di-sulphide. A similar substitute for myrrh is " Bayee balsam," the gum resin furnished by *Balsamodendron pubescens*. The gum left behind in the production of the alcoholic preparations of myrrh is often utilised technically as an agglutinant.

**Analysis.**—The bromine reaction repeatedly advised—and indeed accepted in several Pharmacopœiæ—has been subsequently characterised as unreliable by an equal number of authorities.

If myrrh be extracted with alcohol, and the residue left on evaporation be taken up with ether, bromine vapour is said to give a red-violet colour reaction. Another reaction, also unreliable since it frequently fails, with old or powdered myrrh in particular, is that in which the myrrh is brushed with alcohol and nitric acid, which treatment should give a local cloudy violet coloration. Herabol and Bisabol myrrh are so remarkably different analytically, that the above reaction—which is not given by Bisabol myrrh—is superfluous,

the more so that Bisabol myrrh is at once distinguishable by its odour and appearance, and is, moreover, not met with in commerce at all. Tucholka gives the following reaction for distinguishing between Herabol and Bisabol myrrh :—

" Six drops of a petroleum-ether extract (1 : 15) are mixed with 3 c.c. of glacial acetic acid and floated on the surface of 3 c.c. of concentrated sulphuric acid. A beautiful rose red zone immediately forms at the surface of contact, and after a short time the coloration extends throughout the entire layer of acetic acid, and remains persistent. When a stronger extract is used, a brown coloration is produced. With this reagent the officinal myrrh imparts only a very pale rose coloration to the acetic layer, and the colour does not increase in strength; the surface of contact between the two strata shows at first a green colour, which turns brown with green fluorescence on standing."

Neither bdellium nor Bisabol myrrh gives the bromine vapour reaction furnished by Herabol myrrh; and bdellium can also be readily distinguished from both kinds of myrrh by analytical means (see below).

Hirschsohn examined numerous specimens, and prescribes that the extract in petroleum ether should be colourless, and that it should not exceed 6 per cent. in amount on drying at 120° C., a higher percentage indicating adulteration. The presence of sulphur in these residues is said to point to the presence of bdellium. (In the present state of our knowledge the presence of sulphur compounds in bdellium is dubious, therefore it is not quite clear on what the above inference is based. Asafœtida or sagapenum—both of which contain sulphurous oils—would be more probable, were it not that adulteration with these substances is precluded as too remote.) The petroleum ether should be colourless after the extraction.

Charles E. Escott found 18·75 per cent. soluble in petroleum ether.

The Pharmacopœiæ mostly confine themselves to the bromine reaction, and the prescription of 30 per cent. as a minimum for the amount soluble in alcohol, and 6–8 per cent. for the ash.

The author has found that the percentage soluble in alcohol is greater in Herabol myrrh (up to 50 per cent.) than in Bisabol myrrh (up to 20 per cent.).

Hirschsohn proposed trichloracetal-chloroform as a test for Herabol myrrh. This reagent is prepared by passing chlorine into 75 per cent. alcohol until a turbidity appears and two layers of liquid are formed. The lower liquid is drawn off, washed with water and a little magnesia and filtered. The liquid is trichloracetal; 1 part of this is taken and heated with 4 parts of chloral hydrate till solution is complete. This reagent gives a violet colour with even a very small quantity of Herabol myrrh, but no colour with Bisabol myrrh or any of the other resins.

Kremel found for Herabol myrrh—

| | | I. | II. | III. |
|---|---|---|---|---|
| | Resin . . . . | 39·5% | 42·0% | 23·9% |
| From extract | Acid value (direct) | 64·0 | 60·2 | 70·3 |
| | Ester value . . | 95·0 | 116·5 | 145·8 |
| | Saponification value (hot) | 159·0 | 176·7 | 216·1 |

And for Indian myrrh—

| | | |
|---|---|---|
| | Resin . . . . . | 30·7% |
| From extract | Acid value (direct) . . . . | 42·1 |
| | Ester value . . . . . | 130·8 |
| | Saponification value (hot) . . . | 172·9 |

E. Dieterich found the solubility to be in—

| | |
|---|---|
| Water . . . . | 37·30–52·50 per cent. |
| Alcohol (96 per cent.) . . | 22·6 per cent. |

Tucholka used Kremel's method in his examination of Bisabol myrrh, and, as might have been expected, could not discover any analytical difference between the two kinds of myrrh. The present author examined the same Bisabol myrrh by the method presently to be described, and expressed himself on the subject as follows :—

" As already mentioned in the case of other resins and gum resins, the error of using an alcoholic extract—which point has already been commented upon in the *H. A.*, 1896, p. 126 sec. i.—must be emphasised. This procedure leads to inaccuracy, because, in the first place, alterations take place in the substance itself during the preparation of the extract, besides which an undetermined loss of volatile matter occurs during the concentration of the extract, especially in the case of such gum resins as ammoniacum, galbanum, myrrh, etc., which contain ethereal oils and volatile constituents, the loss varying with the percentage present. The resulting fluctuations are the greater since no account is taken of the degree of solubility in alcohol on the one hand and the percentage of volatile matters on the other, the alcoholic extract being classed as the equivalent of the gum resin itself. When it is remembered that the amount soluble in alcohol is only from 20 to 30 per cent. in the case of Bisabol myrrh, or equal to barely one-third of the total weight of the drug, it can be readily seen that the results obtained are far from corresponding to the entire drug, and what fluctuations the values must therefore be subjected to. In many instances, in place of using a quantity of extract corresponding to 1 grm. of the drug, the values have been determined on 1 grm. of extract; consequently, as this quantity corresponds to much more than 1 grm. of gum resin, the resulting values do not represent the number of mgrms. of KHO fixed by 1 grm. of the drug, but some larger

but unknown quantity, hence the term " acid value " applied to the result has little or no meaning.

" It is therefore not to be wondered at that, on determining the acid and saponification values, Tucholka arrived at results which were unsatisfactory and which did not afford any distinction between the two kinds of myrrh. The divergent and unreliable character of the values obtained, when extracts are used instead of the natural drug, may be gathered from the subjoined figures. Kremel found for Herabol myrrh, with extract, the acid values, 60·2–70·3; ester values, 95·0–148·4; and saponification values, 159–260·1. The author obtained by the same method, from an extract equal to 20 per cent. of the drug, the acid value, 11·2; ether value, 33·6; and saponification value, 44·8. These enormous differences suffice to show how inexact is the examination of extracts, and this is still more clearly evident from the differences found with Bisabol myrrh. Thus Tucholka obtained with an extract the acid value, 55·7; ester value, 87·6; saponification value, 143·3: whilst the author, using an extract equal to a 50 per cent. yield, found the acid value, 5·6; ester value 51·4; and saponification value, 57·00.

" The values turn out very different and much higher when the natural drug is taken for examination, the higher results clearly showing that large quantities of volatile matters are lost during the preparation of the extract, and that the residue insoluble in alcohol also contains acid- and ester-like constituents.

" On the basis of numerous experiments, the author has devised a method which enables the natural drug to be used, and both constituents of the myrrh—the resin soluble in alcohol and the gum soluble in water—to be taken into account."

The method referred to is as follows:—

(*a*) *Acid value* (direct).—One grm. of finely-triturated myrrh, taken as an average sample, is mixed with 30 c.c. of distilled water and warmed for fifteen minutes under a reflux condenser. Fifty c.c. of strong alcohol are added, and the whole is boiled for another fifteen minutes in a steam bath and under a reflux condenser. After cooling, the liquid is titrated with alcoholic $\frac{n}{2}$ potash and phenolphthalein until a true red coloration is produced. The strong alkali is used in preference to the decinormal, because it gives the end-point quicker and more clearly defined. The volume (c.c.) of alkali used multiplied by 28·08 gives the acid value.

(*g*) *Saponification value* (hot).—A further 1 grm. of the average sample is mixed with 30 c.c. of water, left to stand half an hour, then treated with 25 c.c. of alcoholic $\frac{n}{2}$ potash and boiled for half an hour on the steam bath and under a reflux condenser. After cooling and diluting with alcohol it is titrated back, and the volume (c.c.) of KHO consumed multiplied by 28·08 gives the saponification value.

(*c*) *The ester value* is found by difference.

In addition, the percentage soluble in alcohol must be determined by extracting the drug with strong alcohol in a Soxhlet apparatus.

Although, in view of the varying percentage of ethereal constituents, the values furnished by this method are subject to a certain degree of fluctuation, they nevertheless correspond completely to the original drug, especially when care is taken to obtain a true average sample.

The author obtained the following values :—

| Myrrh. | Acid Value (direct). | Ester Value. | Saponification Value (hot). | Per cent. Soluble in Alcohol. |
|---|---|---|---|---|
| Bisabol myrrh . . . | 20·06 | 125·54 | 145·60 | 50 |
| Herabol do. . . . | 25·48 | 204·12 | 229·60 | 20 |

A comparison of the figures obtained by the author with those found by Tucholka in examining extracts shows that this new method is the one which enables the two kinds of myrrh to be distinguished; whereas both kinds exhibit about the same acid value, they differ considerably in the ester and saponification values—the commercial Herabol grade giving far higher figures than Bisabol myrrh.

This peculiarity, in despite of the fact that the percentage of Herabol myrrh soluble in alcohol does not exceed 20 per cent., indicates that the gummy matters soluble in water, that are not included in the old method, contain a greater amount of acid- and ester-like constituents than the alcoholic extract. Special recommendation can be given to the Tucholka qualitative method (see above) in addition to the aforesaid quantitative tests.

When the values given under bdellium are compared with those found for myrrh, it is seen that East Indian and African bdellium gives the lowest and Herabol myrrh the highest figures of these three allied gum resins, whilst Bisabol myrrh occupies an intermediate position.

About eight per cent. should be the highest permissible limit of ash content for officinal Herabol myrrh.

Gregor and Bamberger found the following methoxyl values :—

| | |
|---|---|
| Gregor . . . . . | 13·5 |
| Bamberger . . . . . | 13·2–13·6 |

(For the value of these determinations, see *Chem. Rev.*, 1898, No. 10.)

Mauch estimated the gum in Herabol myrrh by dissolving 1–2 grms. of the gum resin in 10–15 grms. of 60 per cent. chloral hydrate, and weighing the gum thrown down by 100 grms. of strong alcohol. He found 75·2 per cent. of

gum. According to the same authority, this myrrh dissolves to a clear yellow-brown liquid in 8–10 parts of 60 per cent. chloral hydrate.

(On the Germ. Pharm. III. tests for myrrh, see *Ph. C.*, 1898, No. 21.)

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## 50. Olibanum, or Incense.

*Olibanum, Gummi-resina Olibanum.*

**Origin and Habitat.**—*Boswellia Carterii, B. serrata*, and other Burseraceæ. The Somali coast.

**Chemical Constituents.**—According to Braconot it contains: volatile oil, 8; resin, 56; gum, 30; insoluble gum, 5·2; loss, 0·8. Boswellic acid ($C_{32}H_{52}O_4$, M.P. 150°), free and combined as an ester with olibanoresenes $(C_{14}H_{22}O)_n$. Ethereal oil $(C_{10}H_{16})_n$ (pinene, dipentene, phellandrene). Gum, and bitter principle (Tschirch and Halbey). Kurbatow found: resin, 72; gum, 21; volatile oil, 7·0.

**General Properties and Commercial Varieties.**—Small tear-shaped, brittle granules, of dull pale yellow colour, and covered with dust; only partially soluble in alcohol, ether, chloroform, or other solvents. When chewed, the drug breaks down to powder and then softens; the taste is rather bitter and aromatic.

*Olibanum electum* is the best and purest kind, *Olibanum*

*in sortis* being less pure, and corresponding to the *in massa* quality of other gum resins.

The so-called " wild incense," *Olibanum silvestre*, is a pine resin which was formerly employed to adulterate the pure drug. Olibanum, from *Boswellia Freriana* and *B. sacra*, is identical with African elemi (*q. v.*), and is termed " Luban Matti." It should more properly be classed with the elemis and not with the incense group. The resins of other species of *Boswellia*, such as *B. papyrifera*, *B. thurifera*, *B. oblongata*, and *B. socotrana* are similar to olibanum, but are not met with in commerce. Cayenne incense, from *Icica heptaphylla* also belongs to the elemis.

The *Protium* species, such as *P. multiflorum* (" Paú de (incenço " = incense tree), furnish varieties of incense, or substitutes therefor. They are mostly consumed in the interior of Brazil, just as the incense from the Composita *Flourensia thurifera*, is known only in Mexico.

Indian incense is also obtained from a species of *Boswellia* (*B. serrata*), and not, as formerly stated, from *Juniperus Phœnicia*, *J. thurifera*, or *Amyris Kafal*. According to Kosteletzky and Hirschsohn, the name " Indian " is due to the circumstance that the incense was brought to Europe in Indian vessels via Egypt and Arabia. The relatively good concordance of the analytical data, furnished by ordinary and Indian incense, indicates that they are identical.

**Adulterants.**—Colophony, wild incense, mastic, and sandarach.

**Analysis.**—Incense can be distinguished from mastic and sandarach by its odour when heated, its solubility, behaviour when chewed, and by its analytical constants principally that, like amber, it gives saponification values which are not furnished by mastic or sandarach). Numerous analytical data have been published on olibanum.

Hirschsohn examined Arabian, Indian, and African incense, and found the percentage of extract soluble in petroleum ether to amount to 22·08–38·81 per cent. after drying at 120° C. He believes that, as already stated, all the different kinds are referable to the African commercial grade.

The presence of wild incense (pine resin) in olibanum is dealt with as follows in the *Südd. Ap. Ztg.*, 1899, No. 12 :—

" After frequent agitation with water, and leaving at rest for two days, granular incense should leave a white, saccharine mass of resinous constituents, the gum being completely dissolved, whereas an admixture of pine resin will be indicated by the presence of lustrous yellow granules, which may be estimated in an approximately quantitative manner by washing and drying."

Kremel found by the usual method—

| | Resin per cent. | Acid Value (direct). | Ester Value. | Sapon. Value (hot). |
|---|---|---|---|---|
| Olibanum . . | 64·0 | 59·3 | 6·6 | 65·9 |
| Do. . . | 72·1 | 46·8 | 41·0 | 87·8 |
| Do. Indicum . | 67·0 | 50·3 | 60·5 | 110·8 |
| | | | | From extract. |

E. Dieterich also found by the same method—

| | | |
|---|---|---|
| From extract | Acid value (direct) . . . . | 45·40 |
| | Ester value . . . . . | 71·60 |
| | Saponification value (hot) . . . | 117·00 |

The author has used a modified method which enables the natural olibanum to be used instead of an extract. The *modus operandi* is as follows :—

(*a*) *Acid value* (indirect).—One grm. of olibanum is mixed with 10 c.c. of alcoholic and 10 c.c. of aqueous $\frac{n}{2}$ potash, and 50 c.c. of benzine (sp. gr. 0·700). After standing twenty-four hours in a stoppered glass flask, and then adding 500

c.c. of water, the liquid is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The volume (c.c.) of combined KHO multiplied by 28·08 gives the acid value.

(*b*) *Saponification value* (hot).—One grm. of the finely-triturated drug is mixed with 20 c.c. of alcoholic $\frac{n}{2}$ potash, and boiled an hour under a reflux condenser, the liquid being then diluted with 100 c.c. of alcohol and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The volume (c.c.) of combined KHO multiplied by 28·08 gives the saponification value.

(*c*) *Ester value.*—This is found in the usual way, by difference.

(*d*) *Ash content.*—Two grms. of olibanum are carefully incinerated, and calcined until found constant in weight after cooling in a desiccator.

The following values were obtained :—

| | Acid Value (indirect). |
|---|---|
| 1. Olibanum pulvis | 46·20<br>43·40<br>46·20<br>44·80 |
| 2. Do. in granis | 42·00<br>42·00<br>42·00<br>42·00 |
| 3. Do. naturale I. | 50·40<br>46·20 |
| 4. Do. do. II. | 44·80<br>46·20<br>42·00<br>43·30 |
| 5. Olibanum electum | 32·20<br>33·60<br>30·80<br>35·00 |

From these figures it is evident that the *electum* grade, being the purest, gives the lowest acid values, the *pulvis* form yielding the highest values; a circumstance which seems to indicate the adulteration of the latter kind (see also Gamboge).

The advantages of the new method, especially the acid value determination by back titration, consist in the first place in the non-necessity of preparing a solution—which would only occasionally be possible with incense—secondly, in a better and more certain colour-change than in direct titration; and, finally, in the possibility of replacing extract by the natural product.

For the ester and saponification values, the author obtained these figures—

| | |
|---|---|
| Ester value . . . . . | 110–170 |
| Saponification value (hot) . . . | 140–230 |
| Ash . . . . . | traces. |

Using the acid value as a means of detecting adulteration, the subjoined values were obtained :—

| | | Acid Value (indirect). | |
|---|---|---|---|
| 1. | Olibanum + 10 % of dammar . | 47·60 | 47·60 |
| 2. | Do. + 20 % do. . | 46·20 | 46·20 |
| 3. | Do. + 10 % of sandarach . | 58·80 | 56·00 |
| 4. | Do. + 20 % do. . | 58·80 | 57·40 |
| 5. | Do. + 10 % of gallipot . | 65·80 | 65·80 |
| 6. | Do. + 20 % do. . | 74·20 | 71·40 |

Although dammar cannot be detected by this means—and only by the ester and saponification values, which are thereby lowered—the values rise considerably by addition of sandarach or pine resin. If either of these adjuncts be suspected it is advisable to omit the addition of water before titration, in order to avoid the decomposition of the colophony or sandarach soap thereby produced. Information

on this point will be afforded by the Storch-Morawski reaction for colophony (*q. v.*).

The author also found the following degrees of solubility :—

| | |
|---|---|
| In Alcohol . . | partially soluble, leaving white amorphous residue. |
| Ether . . | |
| Benzine . . | |
| Carbon di-sulphide | partially soluble; residue plastic. |
| Chloroform . | partially soluble. |
| Acetone . . | |
| In Glacial acetic acid | for the most part insoluble. |
| Benzol . . | |
| Methyl alcohol . | partially soluble. |
| Amyl do. . | |
| Oil of turpentine | |

Like dammar, amber, and copal, the solubility of olibanum is increased by heat and fusion.

Gregor and Bamberger obtained the following methoxyl values :—

| | |
|---|---|
| Gregor . . . . . | 6·4 |
| Bamberger . . . . . | 5·3 |

Kitt found the carbonyl value = 0·36. (As to the value of these determinations, see *Chem. Rev.*, 1898, No. 10.)

Mauch found that olibanum furnishes only a turbid solution with 60 per cent. chloral hydrate, some time being required for the liquid to clarify. The reason for this is, that the drug contains up to 7 per cent. of ethereal oil, which is only very slowly taken up by the above solvent.

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**Salhar Gum.**—The resin of *Boswellia serrata*, known in India as "salhar" gum, is very similar to ordinary frankincense. A specimen of this material examined at the Imperial Institute gave the following figures:—resin, 53·2 per cent.; gum, 36·45 per cent.; volatile oil, 7·0 per cent.; and ash, 1·55 per cent. It was in the form of rounded tears and irregular masses, and had a turpentiny odour and taste. The gum was entirely soluble in water and behaved similarly to gum arabic. The volatile oil mostly distilled at 175°, but there was a higher boiling-point fraction which did not all distil over below 190°.

## 51. Opopanax.

*Gummi-resina Opopanax.*

**Origin and Habitat.**—There are two distinct varieties—I. Burseracea opopanax, from *Balsamodendron Kafal* (Knuth), Persia; and II. Umbellifer opopanax, from *Opopanax chironium* (Koch), Southern Europe.

Other species of Commiphora yield gum resins similar to opopanax. The Burseracea variety is the kind now in commercial use for perfumery.

### I. Burseracea Opopanax.

**Chemical Constituents.**—Ethereal oil, 6·5 per cent.; gum and vegetable detritus, 70 per cent.; moisture and loss at 100° C., 4·5 per cent.; resin, 19 per cent. The resin consists of chironolic acid ($C_{28}H_{48}O_4$); $\alpha$-panaxresene ($C_{32}H_{54}O_4$); $\beta$-panaxresene ($C_{32}H_{52}O_5$), panaxresinotannol ($C_{34}H_{50}O_8$), an alcohol, chironol ($C_{28}H_{48}O$) (a new type), and bitter principle (Baur).

## II. Umbellifer Opopanax.

**Chemical Constituents.**—Resin soluble in ether, the ferulaic ester of oporesinotannol, 51·80 per cent.; resin insoluble in ether, free oporesinotannol ($C_{12}H_{13}O_2OH$), 1·9 per cent.; gum (a mixture with a formula between that of $C_{12}H_{22}O_{11}$ and $C_6H_{10}O_5$), 33·8 per cent.; ethereal oil, with the oponal ($C_{20}H_{10}O_7$, M.P. 133°–134°) isolated therefrom, 8·3 per cent.; free ferulaic acid ($C_{10}H_{10}O_4$), 0·22 per cent.; vanillin, 0·0027 per cent.; moisture, 2 per cent.; bassorin and vegetable detritus, 2 per cent.; and bitter principle (Knitl).

According to the analysis of Pelletier opopanax contains:—

| | |
|---|---|
| Resin | 42·0 |
| Gum | 33·4 |
| Starch | 4·2 |
| Extractive | 1·6 |
| Wax | 0·3 |
| Malic acid | 2·8 |
| Lignin | 9·8 |
| Volatile oil, etc. | 5·9 |
| | 100·0 |

**General Properties and Commercial Varieties.**—Burseracea opopanax, which at the present time is probably the only variety found in commerce, forms large, brown-yellow lumps, interspersed with paler gummy granules, together with smaller perfectly white lumps. The odour is peculiar, somewhat recalling Sumbul and Bisabol myrrh; some kinds have a wonderfully fine odour, which at once indicates their value for perfumery purposes.

The perfume sold as " opopanax " is said to have nothing to do with the gum resin, but is, according to Holmes, the ethereal oil from *Commiphora Kataf.*

The name " myrrh " has been bestowed on the gum resin by transition from the perfume (coming as this does from a *Commiphora* allied to myrrh), although the gum resin itself, especially the Umbellifer opopanax, has nothing to do with true myrrh.

Umbellifer opopanax when fresh is in greasy masses or brownish yellow lumps, smelling something like levisticum or galbanum—in any case, strong and disagreeable—and with a strongly-bitter balsamic taste.

**Adulterants and Admixtures.**—The two kinds, one for the other; also myrrh, bdellium, and galbanum.

**Analysis.**—Hirschsohn examined several varieties of opopanax, but with such discordant results that the data will not be repeated here.

The author has only recently published sundry analytical particulars of Burseracea and Umbellifer opopanax. As in the case of myrrh, instead of extracts, the natural product was employed, the procedure being as described on p. 408.

The following values were thus obtained :—

| Burseracea Opopanax. | Acid Value (direct). | Ester Value. | Sapon. Value (hot). |
|---|---|---|---|
| 1. | 23·84 | 83·01 | 105·85 |
| | 30·92 | 97·24 | 128·16 |
| 2. | 10·46 | 85·74 | 96·20 |
| | 16·40 | 81·94 | 98·34 |
| 3. | 24·03 | 125·01 | 149·04 |
| | 28·20 | 124·62 | 152·82 |

The following specimens of Umbellifer opopanax, in part obtained direct from Teheran, were also examined :—

| Umbellifer Opopanax. | Acid Value (direct). | Ester Value. | Sapon. Value (hot). |
|---|---|---|---|
| 1. Liquid Teheran opopanax (Jovishir drops) | 32·43 | 105·46 | 137·89 |
| | 33·06 | 119·58 | 152·64 |
| 2. Solid Teheran opopanax (Jovishir dry) | 35·00 | 114·07 | 149·07 |
| | 36·86 | 126·90 | 163·76 |
| 3. Solid opopanax (old) | 53·40 | 142·60 | 196·00 |
| | 58·57 | 140·50 | 199·07 |

The method of analysis is allied to those used for myrrh, bdellium, and sagapenum, but differs considerably from those employed for ammoniacum and galbanum, because the latter are saponified by the cold, or fractionatal, method, whilst the former are saponifiable by the hot process alone. As in the case of galbanum and ammoniacum, a preliminary dissociation of the gum resin is here indispensable. It will be seen from the foregoing tables that Umbellifer opopanax furnishes higher values than Burseracea opopanax.

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## 52. Sagapenum.

*Gummi-resina Sagapenum.*

**Origin and Habitat.**—Not accurately known; at any rate, a Persian Umbellifera. Persia.

**Chemical Constituents.**—Resin soluble in ether, 56·8 per cent.; gum, 23·3 per cent.; water, 3·5 per cent.; impurities, 10·6 per cent.; ethereal sulphurous oil, 5·8 per cent. The pure resin contains: free umbelliferone, 0·11–0·15 per cent.; combined umbelliferone, 15·7 per cent., of which about 40 per cent. is in the form of umbelliferone-sagaresinotannol ester. The sagaresinotannol has the formula $C_{24}H_{27}O_4OH$ (Hohenadl). According to Tschirch

it contains: resin, 57·5 per cent; gum, 23·3 per cent.; essential oil containing sulphur, 19·2 per cent. The resin is free from sulphur and melts at 74°–76°. The essential oil obtained by steam distillation when dissolved in alcohol and treated with HCl, becomes violet in the cold. The oil contains 9·7 per cent. of sulphur, valeric acid, and probably borneol valerate.

**General Properties and Commercial Varieties.**—Dark brown masses, with numerous white lumps, of brittle consistence, turning soft and plastic in the hand. The smell faintly recalls that of galbanum, but also approximates to asafœtida. The ethereal solution gives a red-violet coloration with hydrochloric acid. Sagapenum is soluble in alcohol, ether, alkalis, and sulphuric acid. Formerly the principal commercial varieties were Persian sagapenum "in massa" and Levantine "in tears," but at the present time the drug has almost entirely disappeared from the market.

**Analysis.**—Analytical data are very scarce; it is only recently that the author and Mauch published a few contributions on the subject. The former examined sagapenum by exactly the same method as he applied to myrrh, bdellium, and opopanax, using the crude product instead of an extract (see p. 408).

The following are old analyses of sagapenum:—

| | Pelletier. | Brandes. |
|---|---|---|
| Resin | 54·26 | 50·29 |
| Gum | 31·94 | — |
| Gum with salts of lime | — | 32·72 |
| Volatile oil | 11·80 | 3·73 |
| Bassorin | 1·00 | 4·48 |
| Malate of lime | 0·40 | — |
| Malate and phosphate of lime | — | 1·12 |
| Peculiar matter | 0·60 | — |
| Impurities | — | 4·30 |
| Water | — | 4·60 |
| | 100·00 | 100·00 |

The author obtained the following values with the crude product :—

| | I. | II. |
|---|---|---|
| Acid value (direct) . . . | 13·96 | 14·81 |
| Ester value . . . . . | 31·29 | 39·37 |
| Saponification value (hot) . . | 45·25 | 54·18 |

Mauch found sagapenum to contain umbelliferon, and to dissolve, as a brown liquid, in 60 per cent. chloral hydrate. Like galbanum, sagapenum gives all the reactions for umbelliferon.

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